TIGHT BINDING BOOK

A SHORT MANUAL OF SYSTEMATIC QUALITATIVE ANALYSIS

BY MEANS OF MODERN DROP REACTIONS

BY

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AND

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3RD EDITION

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Abbreviations:

prec. = precipitate.
sol. = soluble.
conc. = concentrated.
dil. = dilute.

PREFACE.

In the course of the last ten years, analytical practice has been enriched by a great many very sensitive and often very specific reagents due to the important investigations of FEIGL, TANANAEFF, EEGRIWE, HAHN, KOLTHOFF and others. For the greater part these reagents are of an organic nature. The reactions in some are due to catalytic effects and a large number are sensitive even to a semi-microchemical scale. Nevertheless up to the present time only a few of them have entered into general courses of systematic qualitative analysis.

This short manual pretends to give a slightly modified systematic course specially devised to allow of an effective use of modern drop reactions for identification purposes. In our opinion, the weakest point in analytical practice has been the almost total neglect of the drop reactions. We do not pretend our scheme of separations to the best possible, nor do we claim our choice of drop reactions to be the most delicate. Indeed we know they are not, but we give *a scheme and a set of reactions*, which have given us satisfaction *as a whole* during three trial years with some hundreds of students.

At the same time we deviate more or less from the usual technique. Instead of the usual test tube we systematically employ a porcelain drop plate or a microscope object glass. Filtering apparatus has been replaced by a centrifuge, which saves a great deal of time and moreover brings precipitates together instead of spreading them all over a paper. We have not been unmindful of the advantages of the microchemical technique evolved by BEHRENS, in consequence of which much of the procedure has been reduced to a semi-microchemical scale. In this way much time is gained by the student, accuracy is increased and his style greatly improved.

We do not aim at all at the detection of traces, a problem wholly apart from ordinary qualitative routine; nor do we aim, like some others, at the detection of ions with as small a number of separations as possible. The didactical importance of separations is far too great for that. Our only purpose is

to give a modern laboratory manual — for college students in the first place, but just as well for analytical work outside college practice — aiming at an improvement of the ultimate identification and consequently at a strengthening of self-confidence.

In our earlier experiments we tried quite a number of modern systematic separations without the use of hydrogen sulphide, however without any success. We are convinced, that the old H_2S-method is still the most accurate and the most reliable one.

We shall always be glad to receive suggestions for improvements and information about results obtained.

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Preface to the 2nd edition.

Some new reactions have been added and here and there some alterations have been made. For the separation of the alkaline earths, the "old" $(NH_4)_2CO_3$-method has been taken up as an alternative, when the detection of small amounts of these elements is not aimed at.

Our sincere thanks are due to a great many of our colleagues and collaborators for valuable advice and to Mr. J. SANDILANDS from Heriot-Watt College, Edinburgh, who revised the proofs of this edition.

Delft, 1935.   v. N.-D.

Preface to the 3rd edition.

Awaiting the publication of the Report of the Committee on New Reagents of the International Union of Chemistry, which will give us a better survey of the avaitable spot tests, we thought is best to introduce no new reactions. This edition is essentially the same as the second. The abbreviation "cc" has been replaced by "ml".

Delft, 1938.   v. N.-D.

GENERAL REMARKS.

TO BE READ VERY CAREFULLY BEFORE BEGINNING WORK!

1. The secret of successful qualitative analytical practice is:
   a. to observe and to interpret details.
   b. to develop and to cultivate a "style".
   c. to operate on as small quantities as possible.

2. For observing details it is necessary to have imprinted on one's mind a thorough knowledge of the principal facts relating to the phenomena which are at all possible: the solubility of different types of salts and bases: the solubility of the latter in an excess of alkali hydroxide or ammonia and generally the physical and chemical characteristics of substances. However uninteresting this may be, it is essential that this part of the study be completed before beginning analytical laboratory work.

3. For succesfully interpreting results, a working knowledge of theoretical chemistry is indispensable. The principles of the law of mass action, the equilibrium law of van 't Hoff-Le Chatelier, solubility products, the ionisation theory and the elements of colloidal chemistry should be studied.

4. Try to develop your own "style", i.e. always carry out the same operations in the same way, of course in one of the many good ways. Only then primitive "qualitative" routine work is changed to "semi-quantitative" work, which is the only true method! For only then you get an insight into the effects caused by traces of other ions and by the unavoidable incompleteness of the separation schemes.

5. For the complete analysis of mixtures containing some five to ten kations and some anions, inexperienced wor-

kers should use about 300 mgrs of substance. In the course of time however, this quantity could be decreased to about 100 mgrs. Usually drop reactions work best when small quantities are employed and from 20-50 γ is the amount generally aimed at. ($\gamma = 0.001$ mgr.) Never use a test tube when a drop plate or an object glass could be used; ignition of material in the loop of a platinum wire can often be employed in place of ignition in a crucible.

6. Carefully note all your observations and interpretations in a laboratory journal, never on loose papers! Do not depend only on the final identification reactions, but try to arrive at definite conclusions, positive as well as negative, as soon as possible.

7. Keep your laboratory materials in a meticulously clean state, always completely ready for immediate use.

8. As a rule, the liquids, used for washing out precipitates, are not added to the rest of the substance under examination. At most the first wash liquid can be kept.

9. Always try beforehand with a small portion of the available material, whether a certain operation is necessary at all.

10. Arrange your work in such a way, that you can perform one operation while waiting for the result of another one!

11. Have regard to your neighbours safety as well as your own.

CHAPTER I.

The analytical characteristics of the more important KATIONS.

SILVER.

Monovalent, Kation Ag·.

1. Alkali hydroxides give a brown prec. of Ag_2O, aq, not amphoteric, not soluble in an excess.
2. Ammonia gives the same prec. but easily soluble in an excess of NH_3 by formation of 'complex silver-ammonia kations.
3. Chloride ions give a white prec. of AgCl, insol. in HNO_3, sol. in NH_3 (complex kations), in KCN and in thiosulphates (complex anions).
4. Bromide- and iodide ions give similar prec.; AgBr is pale yellow and only sparingly sol. in NH_3; AgI is bright yellow and insol. in NH_3.
5. Hydrogen sulphide gives a black prec. of Ag_2S, insol. in dilute mineral acids. Sol. in hot dilute HNO_3 with separation of S.
6. Reducing agents, especially in alkaline solutions, reduce to free Ag.
7. Chromate ions give a red-brown precipitate of Ag_2CrO_4, sol. in dil. HNO_3 and in NH_3.

DROP REACTIONS:

a. A stain of AgCl (from Ag· and Cl′) on a filter paper is coloured black by addition of $MnSO_4$ and KOH. (TANANAEFF) [1])

> The black colour of Ag is not to be confused with the brown colour of oxidised $Mn(OH)_2$. Mercury gives a similar reaction but cannot be present when AgCl has been prepared by a previous extraction with NH_3.

b. A suspension of fresh AgCl in dilute HCl is coloured rose by an acetone solution of dimethylaminobenzylidene-rhodanine (rhodanine reagent,

HN——C=O
| |
S=C C=CH ⟨═⟩ N(CH₃)₂ (FEIGL) [2])
\ /
S
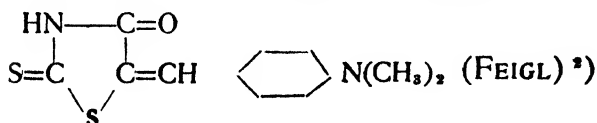
With a trace of amyl alcohol, the colour is conc. in the films of this substance. With very small amounts of Ag, the excess of the reagent may be removed with acetone. Mercury gives the same reaction, but prevented by KCN.

ARCENIC.

A. P e n t a v a l e n t, Kation As^V, anion AsO_4'''.

The equilibrium $As^V + 5OH' \rightleftharpoons ASO_4''' + 3H^{\cdot} + H_2O$ is situated extremely on the righthand side; so reactions of the As^V ion can only be expected in very strongly acid solutions.

1. A l k a l i h y d r o x i d e s and N H$_3$ give no prec.
2. H y d r o g e n s u l p h i d e gives a prec. only in moderately strongly acid solutions. The yellow prec. is As_2S_5, insol. in HCl 1 : 1, sol. in KOH and in $(NH_4)_2S$ by formation of sulpho-arsenates. When H_2S is passed through a weakly acid hot solution of arsenates, after some time As_2S_3 is precipitated together with S.
3. P o t a s s i u m i o d i d e reduces As^V solutions only in an acid medium. On the other hand $As^{\cdots}$ solutions are oxidised by iodine in an alkaline medium.
4. Arsenates generally give the same precipitation reactions as PO_4''' ions.

B. T r i v a l e n t, Kation $As^{\cdots}$, anion AsO_3'''.

The equilibrium between $As^{\cdots}$ and AsO_3''' is as with As^V, only less extreme. So here also reactions of the $As^{\cdots}$ ion can only be expected in strongly acid solutions.

1. A l k a l i h y d r o x i d e s and N H$_3$ give no prec.
2. H y d r o g e n s u l p h i d e in acid solution gives a yellow prec. of As_2S_3, insol. in HCl 1 : 1, sol. in KOH and in $(NH_4)_2S$ by formation of sulpho-arsenites.
3. P o t a s s i u m i o d i d e in conc. HCl gives an orange-red prec. of AsI_3, decomposed by dilution. Very sensitive and specific.
4. C u p r i c s u l p h a t e and K O H give a green prec., sol. in an excess of KOH with a blue colour; when boiled, red-brown Cu_2O is prec.

In the same way a great many other substances are reduced by AsO_3''' ions.

SENSITIVE REACTIONS FOR SMALL AMOUNTS OF AS.

a. Stannous chloride in conc. HCl gives a brown solution, probably caused by free As. (BETTENDORF)[3])

b. All arsenic compounds (the sulphides excepted) are reduced to AsH_3 when treated with Zn or Al and a mineral acid. The presence of AsH_3 may be detected by means of a minute crystal of $AgNO_3$ (GUTZEIT SR)[4]), a drop of $AuCl_3$ (WINKLER)[4a]) or a drop of $HgCl_2$ (SANGER-BLACK)[4b]) on a filter paper after removal of H_2S with Pb-acetate. However, this procedure is rather dangerous, because SbH_3 gives quite similar reactions. Therefore, we prefer to reduce the As-compounds, not in an acid, but in an alkaline medium, i.e. by means of Al shavings and 2N KOH. Under these circumstances Sb-compounds are reduced to metallic Sb, and pentavalent As-compounds are not reduced at all. It is true, that in this way, the As-reaction becomes slightly less sensitive (which is sometimes an advantage in itself), but now it is specific so long as H_2S and PH_3 are absent.

> The reaction is best carried out in a small test tube, with a wad of cotton wool, moistened with Pb-acetate and a filter paper with a drop of $HgCl_2$ on top. Gentle heating: brown stain. It is essential to use a very pure brand of Al shavings, free from As and P. Always carry out a blank.

c. See the reaction sub B, 3, which is very sensitive, especially when carried out under the microscope. As may be separated from the rest by volatilization as As_2O_3.

ANTIMONY.

A. P e n t a v a l e n t, Kation Sb^V, anion SbO_4'''.

The equilibrium between Sb^V and SbO_4''' is not so extremely on the right hand side as with As. This is equivalent to saying, that Sb has somewhat more the character of a metal.

1. W a t e r, i.e. dilution, has no effect (distinction from Sb$^{...}$).

2. A l k a l i h y d r o x i d e s and N H$_3$ can give a white prec. (H$_3$SbO$_4$) from not too dilute solutions, sol. in an excess of KOH, only sparingly in NH$_3$. Under favourable conditions, NaOH may form the insol. salt Na$_2$H$_2$Sb$_2$O$_7$.

3. H y d r o g e n s u l p h i d e in cold solutions gives an orange prec. of Sb$_2$S$_5$, in hot solutions a mixture of Sb$_2$S$_5$, Sb$_2$S$_3$ and S, soluble in HCl 1 : 1, with a residue of S. Only trivalent Sb is in solution. Soluble in KOH and in (NH$_4$)$_2$S by formation of sulpho-antimonates.

4. P o t a s s i u m i o d i d e reduces an acid solution of Sb^v to Sb$^{...}$. In an alkaline medium iodine oxidises antimony from Sb$^{...}$ to Sb^V.

B. T r i v a l e n t, Kations Sb$^{...}$ and SbO$^{.}$ (antimonyl), anion SbO$_3$$^{'''}$.

1. W a t e r, i.e. dilution, often causes the prec. of insol. antimonyl compounds, especially SbOCl.

2. A l k a l i h y d r o x i d e s and N H$_3$ give a white prec. of H$_3$SbO$_3$, soluble in an excess of hydroxide, only sparingly in NH$_3$.

3. H y d r o g e n s u l p h i d e in acid solution gives an orange prec. of Sb$_2$S$_3$, soluble in HCl 1 : 1, in KOH and in (NH$_4$)$_2$S by formation of sulpho-antimonites.

4. S o d i u m t h i o s u l p h a t e, when added in a small amount to a very weakly acid solution of Sb$^{...}$ gives an orange-red prec. (of Sb$_2$S$_2$O?). Oxalic acid does not prevent the reaction (as with Sn).

5. Z i n c and a l u m i n i u m reduce to SbH$_3$ (gaseous), but only in an acid medium. SbH$_3$ may be detected in the same way as AsH$_3$.

6. T i n and i r o n reduce an acid Sb$^{...}$ solution to metallic Sb, which separates as black flakes if the solution is not too acid (distinction from Sn).

DROP REACTION:

Sb^V solutions (obtained from Sb$^{...}$ by means of KNO$_2$ and HCl) in HCl 1 : 1 turn the pink solution of rhodamine-B into bluish-violet. (EEGRIWE)[5])

> Rhodamine-B is a triphenylmethane dye. Molybdates and especially tungstates give similar reactions. An excess of nitrite must be avoided. The reagent is best dissolved in HCl 1 : 1 with KCl as a buffering agent.

TIN.

A. Tetravalent, Kation Sn^{IV}, anion SnO$_3''$.

1. Alkali hydroxides and NH$_3$ give a very gelatinous, white prec. of SnO$_2$, aq, very easily remaining in colloidal solution; when fresh, it redissolves in HCl and in an excess of KOH, only sparingly in NH$_3$. When boiled for some time, or when prepared from tin and nitric acid (metastannic acid), the SnO$_2$, aq, especially after drying, is only very slowly attacked by KOH and by HCl.

2. Hydrogen sulphide in dilute acid solutions gives a yellow prec. of SnS$_2$, sol. in HCl 1 : 1; sol. in KOH and in (NH$_4$)$_2$S by formation of sulpho-stannates.

3. Iron and aluminium reduce an acid solution of Sn^{IV} to Sn$^{..}$ (distinction from Sb), which may be detected by its reducing power.

B. Bivalent, Kation Sn$^{..}$, anion SnO$_2''$.

1. Alkali hydroxides and NH$_3$ give a white prec. of Sn(OH)$_2$, sol. in an excess of KOH, insol. in NH$_3$; the solution in KOH (stannite) is decomposed by boiling for a long time, forming Sn and stannate.

2. Hydrogen sulphide in dilute acid solution gives a prec. of brown SnS, not easily soluble in KOH and in colourless (NH$_4$)$_2$S, but soluble in polysulphides, forming sulpho-stannates.

3. Mercury chloride is reduced by SnCl$_2$, first to Hg$_2$Cl$_2$, later to Hg.

DROP REACTION:

A stannous solution, obtained by reducing Sn^{IV} with Al shavings, reduces a solution of cacotheline (an oxynitro-brucine), turning its colour from yellow into a brown-violet. Antimonous and ferrous *) salts do not show this reaction! (DRYER[6]), GUTZEIT JR.[7])).

> Heating helps the reaction. H_2S also reduces the reagent, so this must be effectively removed by boiling. All particles of undissolved aluminium must also be removed by filtration for the same reason. Titanous compounds may interfere.

COPPER.

A. B i v a l e n t, Kation $Cu^{..}$.

1. A l k a l i h y d r o x i d e s give a bluish prec. of $Cu(OH)_2$, which turns black when boiled with an excess of KOH. Somewhat sol. in a large excess of conc. KOH (colloidal solution?).

2. A m m o n i a gives a similar prec.; it is very easily sol. in an excess of NH_3, forming complex copper-ammonia kations of an intense blue colour. Sensitive reaction, but not specific because of nickel!

3. H y d r o g e n s u l p h i d e in acid solution gives a black prec. of CuS, insol. in dilute mineral acids, in KOH, or in Na_2S, but perceptibly in amm. polysulphide. In the course of time it decomposes into Cu_2S and S, and moreover it is oxidised in contact with air to soluble $CuSO_4$.

4. P o t a s s i u m i o d i d e gives a prec. of Cu_2I_2 with liberation of iodine.

5. P o t a s s i u m f e r r o c y a n i d e gives a brown prec., insol. in dilute acids, sol. in NH_3.

6. P o t a s s i u m s u l p h o c y a n a t e and H_2SO_3 gives prec. of $Cu_2(CNS)_2$. (Distinction from Cd).

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*) Provided F'- and PO_4'''-ions are absent; c.f. FEIGL, Tüpfel-reaktionen, 2te Aufl., p. 46.

DROP REACTION:

 a. When traces of $Cu^{..}$ are present, the prec. of $ZnHg(CNS)_4$ from zinc sulphate and $(NH_4)_2Hg(CNS)_4$ solutions is coloured from violet to black. Specific and exceedingly sensitive. (MONTEQUI) [8])

  The reaction succeeds only with traces of $Cu^{..}$. It is essential that $Cu^{..}$ is present beforehand. Addition of $Cu^{..}$ to a prec. of $ZnHg(CNS)_4$, once formed, has no effect at all. We prefer this reaction to all other drop reactions of $Cu^{..}$, which are innumerable.

 b. Neutral solutions of cupric salts give a green prec. with an alcoholic solution of benzoinoxime (FEIGL) [8a])

  The reagent is $C_6H_5.CH(OH).C(:NOH).C_6H_5$. The reaction is specific for Cu, and best carried out on filter paper. Develop over NH_3.

B. Apparently monovalent, in reality b i v a l e n t ion $Cu_2^{..}$.

 1. A l k a l i h y d r o x i d e s give a red-brown prec. of Cu_2O, aq, insol. in an excess.

 2. A m m o n i a gives a similar prec.; it is sol. in an excess of NH_3 to a colourless solution, containing complex cuprous-ammonia kations. The solution is very sensitive to traces of air.

 3. Cu_2Cl_2, white, is insol. in water, but sol. in conc. HCl (complex anions) and in NH_3 (complex kations).

BISMUTH.

 Trivalent, Kations $Bi^{...}$ and $BiO^{.}$.

 1. A l k a l i h y d r o x i d e s and NH_3 give a white prec. of $Bi(OH)_3$, insol. in an excess.

 2. C h l o r i d e i o n s give a white prec. of BiOCl when the acidity is low enough. The same prec. is formed when an acid solution of $BiCl_3$ is diluted.

 3. H y d r o g e n s u l p h i d e in acid solution gives a brown prec. of Bi_2S_3, insol. in KOH and in $(NH_4)_2S$.

 4. P o t a s s i u m i o d i d e gives in a conc. $Bi^{...}$ solution a black prec. of BiI_3, in a dilute solution an orange prec. of BiOI. Both are sol. in an excess of KI.

5. P h o s p h a t e s give a white prec. of BiPO$_4$, insol. in dilute nitric acid (max. strength 0,2 normal).

DROP REACTIONS:

a. Traces of Bi-compounds have a very marked accelerating effect on the reduction of a plumbite by means of a stannite solution, causing a prec. of Pb. (FEIGL and KRUMHOLZ) [9])

> This is a modification of a well known reaction of Vanino. Large amounts of Bi are readily reduced to Bi by K$_2$SnO$_2$. Lead acetate is only reduced after a very long time. When however traces of Bi are present, the reduction of lead is catalytically accelerated. So the formation of a prec. of Pb is an indication for the presence of Bi.

b. A solution of cinchonine nitrate and potassium iodide is coloured orange with traces of a Bi-solution. (LÉGER) [10])

> Lead gives also a prec., but more of a yellow colour.

LEAD.

Bivalent, Kation Pb$^{..}$, anion PbO$_2''$; sometimes tetravalent anion PbO$_3''$.

1. A l k a l i h y d r o x i d e s and N H$_3$ give a white prec. of Pb(OH)$_2$, sol. in an excess of KOH, forming plumbites, insol. in on excess of NH$_3$.

2. H y d r o g e n s u l p h i d e gives a black prec. of PbS, insol. in KOH and in (NH$_4$)$_2$S, appreciably sol. in amm. polysulphide. It is perceptibly sol. in mineral acids stronger than about half normal.

3. S u l p h a t e i o n s give a white prec. of PbSO$_4$, appreciably sol. in conc. mineral acids. Also sol. in a great excess of KOH and in a hot and conc. solution of amm. acetate, forming complex lead acetate anions.

4. C h r o m a t e i o n s give a yellow prec. of PbCrO$_4$, sol. in warm dil. HNO$_3$ and in an excess of KOH.

5. C h l o r i d e i o n s give a white prec. of PbCl$_2$ from

not too dilute solutions, sol. in hot water and in conc. HCl (complex anions).

6. I o d i d e   i o n s give a yellow prec. of PbI_2, sol. in an excess of conc. KI-solution.

7. A l k a l i n e   o x i d i s i n g   a g e n t s like KOH and H_2O_2 or persulphate and NH_3 give a brown prec. of PbO_2,aq or plumbates.

DROP REACTION:

PbO₂ or plumbates, after addition of amm. chloride and acetic acid, give a blue colour with a sol. of tetramethyl-diamino-diphenyl-methane. (TRILLAT) [11])

> The reagent is $CH_2[C_6H_4N(CH_3)_2]_2$. It will be oxidised by some peroxides, not by H_2O_2. The removal of the supernatant liquid is necessary however, because PbO_2 together with H_2O_2 is decomposed in an acid solution. Bismuth and thallium give the same reaction. So these must be separated from lead by sulphuric acid.

CADMIUM.

Bivalent, Kation Cd¨.

1. A l k a l i   h y d r o x i d e s give a white prec. of $Cd(OH)_2$, insol. in an excess.

2. A m m o n i a may give basic salts or the same prec., but it is very easily sol. in an excess of NH_3, forming complex cadmium-ammonia kations.

3. H y d r o g e n   s u l p h i d e gives a yellow prec. of CdS, insol. in KOH and in $(NH_4)_2S$, but sol. in warm H_2SO_4 (1 : 5) (distinction from Cu). The prec. with H_2S is complete only when the acidity of the solution is less than 0,25 normal.

4. When Cd-compounds, if necessary mixed with soda, are reduced in a very small tube either with charcoal or with coal gas, the element is formed. This is very volatile and condenses in the colder parts of the tube as a mirror with a brown seam of CdO. When then some sulphur is distilled over the mirror, it turns

orange when hot, yellow when cold. This is the best way for detecting small amounts of cadmium. (GEILMANN) [12])

MERCURY.

A. B i v a l e n t, Kation $Hg^{..}$.

1. A l k a l i h y d r o x i d e s give a yellow prec. of HgO, aq, insol. in an excess.

2. A m m o n i a gives a white prec. of somewhat variable composition, e.g. $HgNH_2Cl$. When much NH_4 salt is present, the prec. is incomplete.

3. H y d r o g e n s u l p h i d e in acid solution gives — via yellow and brown intermediate compounds — a black prec. of HgS, insol. in KOH (when As, Sb and Sn are absent) and in $(NH_4)_2S$, insol. in hot HNO_3 1 : 1 (distinction from Bi, Pb, Cu and Cd), but sol. in Na_2S-solutions, forming sulpho-mercurate, from which it is reprecipitated by NH_4Cl.

4. I o d i d e i o n s give a yellow-red prec. of HgI_2, soluble in an excess of KI and in an excess of $HgCl_2$.

5. C y a n i d e i o n s react with $Hg^{..}$-compounds, forming $Hg(CN)_2$, soluble in water, but so extremely little ionized, that it does not show the ordinary $Hg^{..}$-reactions (exepted the reaction with H_2S). $HgCl_2$ is also only little ionized, though far more than $Hg(CN)_2$.

6. S t a n n o u s c h l o r i d e gives a white prec. of Hg_2Cl_2, after some time grey Hg.

7. M e t a l l i c c o p p e r separates mercury as a grey stain on the metal. After drying the mercury can be distilled off in a very small test tube and condensed in the cold parts of the tube as small drops. (Specific, and, after some experience, a sensitive reaction!)

B. Apparently monovalent, in reality b i v a l e n t, Kation $Hg_2^{..}$.

1. A l k a l i h y d r o x i d e s give a black prec. of either Hg_2O, aq or HgO, aq and Hg, insol. in an excess.

2. A m m o n i a gives a black prec. of variable composition, e.g. Hg_2NH_2Cl or $HgNH_2Cl$ and Hg.

3. H y d r o g e n s u l p h i d e gives a black prec., Hg_2S or HgS and Hg.

4. C h l o r i d e i o n s give a white prec. of Hg_2Cl_2.

DROP REACTIONS :.

a. Ionized mercury solutions give in a neutral or slightly acid solution (HNO_3) a blue colour with symm. diphenylcarbazide. (CAZENEUVE [13]), ODDO [14]))

> The reagent, $O = C (NH—NHC_6H_5)_2$, has been introduced by Cazeneuve (also for chromates). In alkaline solutions it shows a bright red colour, so an excess of alkali must be avoided. Copper gives a similar reaction. So when Cu was present, the reaction sub b, is better employed for the detection of mercury. Au and Pt interfere.

b. When a solution of mercury salts is treated with stannous chloride and aniline a black or dark brown prec. is obtained. (TANANAEFF) [15])

> This reaction is best carried out on a filter paper. Both mercurous and mercuric salts give the reaction.
> Ag, Au and Pt interfere, copper does not.

URANIUM.

Hexavalent, Kations U^{VI} and $UO_2^{··}$ (uranyl), anions UO_4'' and U_2O_7''. Moreover tetravalent $U^{····}$.

1. A l k a l i h y d r o x i d e s and N H 3 primarily give a yellow prec. of $UO_2(OH)_2$; this is amphoteric, forming uranates, mostly pyrouranates, with an excess of KOH, NaOH or NH_3, but these uranates are insoluble just as well.

2. A m m o n i u m s u l p h i d e gives a dark brown prec. of UO_2S, sol. in dilute mineral acids.

3. A m m o n i u m c a r b o n a t e dissolves all uranium compounds (incl. UO_2S), forming very stable complex uranyl-carbonate anions. These are decomposed only by boiling with an excess of HCl.

4. P o t a s s i u m f e r r o c y a n i d e gives a brown prec.

(like Cu and Mo). With NH_3 it turns yellow (Cu turns blue, Mo colourless).

ALUMINIUM.

Trivalent, Kation $Al^{...}$, anions $AlO_3^{'''}$ and $AlO_2^{'}$.

1. **A l k a l i h y d r o x i d e s** give a white prec. of $Al(OH)_3$, sol. in an excess. It can be reprecipitated by exact neutralization at $p_H = 8—9$.

2. **A m m o n i a** gives the same prec., insol. in an excess of ammonia.

3. **A m m o n i u m s u l p h i d e** contains so much OH'-ions, that it also prec. $Al^{...}$-solutions as $Al(OH)_3$.

4. **A l k a l i a c e t a t e s** only prec. hot solutions of $Al^{...}$ as a basic Al-acetate. When cooling, the prec. can partly redissolve.

5. **P h o s p h a t e s**, when the acidity is low enough, give a white prec. of $AlPO_4$, sol. in dilute mineral acids, but insol. in acetic acid (distinction from Ca, Sr, Ba and Mg). It is also sol. in KOH.

DROP REACTIONS:

a. The violet-red mordant dye, formed when an acid solution of alizarin-S and an Al-salt is made ammoniacal, is turned red-brown by the action of dilute acetic acid. Without Al the original yellow colour of alizarin-S comes back again. Exceedingly sensitive. (ATACK) [16])

> The reagent is the sodium salt of alizarin sulphonic acid. Ferric salts interfere with this detection of Al, so the separation of Fe and Al must be carried out carefully. Chromium salts, even in large excess, do not interfere. The reaction is carried out on pure filter paper (blank). Be, Ti, Zr and the rare earths give the same reaction. When these are present, the best Al-reaction is the microchemical detection as Cs-Al-alum.

b. Approximatively neutral or slightly acetic acid $Al^{...}$-solutions turn a yellow, alcoholic solution of morine

into a bright, fluorescent green. The reaction takes some time. (GOPPELSRÖDER) [17])

Be¨ gives the same reaction.

CHROMIUM.

A. T r i v a l e n t, Kation Cr···.

1. A l k a l i h y d r o x i d e s give a greyish-green prec. of Cr(OH)₃, feebly amphoter, sol. in an excess of cold KOH, from which solution it is reprec. by boiling.

2. A m m o n i a and amm. sulphide give the same prec., sol. in an excess of cold ammonia, insol. in hot ammonia.

3. A l k a l i a c e t a t e s, either cold or boiling, give no prec. When however much Fe··· or Al··· is present, Cr··· is coprecipitated.

4. P h o s p h a t e s give a prec. of CrPO₄, sol. in dilute mineral acids, sol. in cold dilute acetic acid, but insol. in hot, dilute acetic acid.

5. When molten with soda and NaNO₃ (or even without NaNO₃), chromium compounds are transformed into sodium chromate, which dissolves in water with a yellow colour. Specific reaction.

B. H e x a v a l e n t, Anions CrO₄″ and Cr₂O₇″.

1. O H ′ - i o n s turn the red Cr₂O₇″-ion into yellow CrO₄″. H · - i o n s bring about the reserve reaction.

2. B a r i u m and l e a d i o n s give a yellow prec., sol. in dilute mineral acids, insol. in acetic acid.

3. H y d r o g e n p e r o x i d e and an excess of very dilute sulphuric acid gives a bright blue perchromic acid, soluble in ether.

DROP REACTION:

Chromates give a bright violet colour with diphenyl-carbazide in dilute sulphuric acid solution. (CAZENEUVE) [18])

As many other oxidising agents give the same reaction, and as a rule the chromates are prepared from Cr···-compounds by alkaline oxidation, e.g. with KOH and

bromine, it is necessary to remove the excess of bromine with phenol and sulphuric acid. Ferric salts give a similar reaction, but not in a moderately strong acid medium.

IRON.

A. B i v a l e n t, Kation $Fe^{..}$.

1. A l k a l i h y d r o x i d e s and NH_3 give a pale green prec. of $Fe(OH)_2$, insol. in an excess of the reagents; in contact with air it oxidises rapidly to brown $Fe(OH)_3$. Presence of NH_4-ion prevents complete precipitation.

2. A m m o n i u m s u l p h i d e gives a black prec. of FeS, very easily sol. in dilute HCl.

3. P o t a s s i u m f e r r i c y a n i d e gives a blue prec. in acid solutions; sol. in oxalic acid.

B. T r i v a l e n t, Kation $Fe^{...}$.

1. A l k a l i h y d r o x i d e s and NH_3 give a complete prec. of $Fe(OH)_3$, also when ammonium salts are present. The prec. is insol. in an excess of the reagents.

2. H y d r o g e n s u l p h i d e causes reduction to $Fe^{..}$ with the separation of S when the reaction is carried out in an acid medium.

3. A m m o n i u m s u l p h i d e gives a black prec., either Fe_2S_3 or FeS and S, according to circumstances, both easily sol. in dilute HCl.

4. P o t a s s i u m f e r r o c y a n i d e gives a blue prec. in acid solutions.

5. S u l p h o c y a n a t e s give a red colour in acid solutions. Colour is discharged by F', $SnCl_2$, $HgCl_2$ etc. Very sensitive and moreover specific (molybdates give the same colour only when reducing agents are present at the same time).

6. A l k a l i a c e t a t e s give a red-brown colour in acid solutions. When diluted and boiled for a brief period, $Fe^{...}$ is completely prec. as a complex basic ferric acetate.

7. **P h o s p h a t e s** give a prec. of $FePO_4$ in sufficiently weak acid solutions, sol. in dilute HCl, insol. in acetic acid.

a_1. Ferrous salts in neutral or slightly ammoniacal solution give a red solution (but never a prec.; distinction from Ni) with dimethylglyoxime. (SLAWIK) [10])

a_2. Ferrous salts in dilute acid solution give a red colour with α, α'-dipyridyle (BLAU, FEIGL and HAMBURG) [10a])
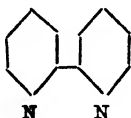
The reagent is It is rather expensive and best dissolved in alcohol. A large excess of mineral acid must be avoided.

b. Ferric salts are best detected by means of the sulpho-cyanate reaction (see B,5).

Ions, which form stable complexes with $Fe^{...}$, such as tartrates, phosphates, fluorides etc. ought to be absent. Nitrites must be absent just as well, because they can give rise to the formation of CNSNO, which has a colour similar to $Fe(CNS)_3$.

COBALT.

Bivalent, Kation $Co^{..}$; in the hydroxide and in a great many complex ions, the trivalent cobalt is more stable.

1. **A l k a l i h y d r o x i d e s** give a bluish-rose prec. of basic salts or $Co(OH)_2$, which, when freshly prepared, is appreciably sol. in an excess of KOH. When moreover some bromine water or H_2O_2 is added, and even in prolonged contact with air, black $Co(OH)_3$ is formed, quite insol. in an excess of KOH.

2. **A m m o n i a** also gives a prec. of $Co(OH)_2$, which partly as such dissolves into an excess of ammonia, partly, by contact with air, as the very stable cobalti-ammonia-complexes. Neither KOH alone nor KOH and bromine water give prec. with these cobalti solutions (distinction from Ni). Cobalto hydroxide is moreover considerably sol. in ammonium salts.

3. A m m o n i u m   s u l p h i d e gives a black prec. of CoS; hydrogen sulphide in dilute mineral acid solution does not. Nevertheless CoS, once precipitated, is insoluble in dilute HCl (1 : 10).

4. P o t a s s i u m   n i t r i t e in very dilute acetic acid solution gives after some time a yellow crystalline prec. of $K_3Co(NO_2)_6$. (Distinction from Ni).

DROP REACTIONS:

a. An alcoholic solution of $Co^{..}$ salts, often already blue of itself, gives a bright blue colour with a crystal of KCNS or NH_4CNS. (SKEY [20]), VOGEL [21]))

> To an aqueous solution at least three volumes of ethyl alcohol are added. The use of amyl alcohol is superfluous. Very useful and specific reaction, provided $Fe^{...}$ is absent. However iron may be made in offensive by $SnCl_2$, by tartaric acid, or by fluorides.

b. α-Nitroso- β-naphtol gives a reddish brown colour in acetic acid solution, not removed by 2N HCl. (ILINSKY and v. KNORRE) [22])

> This reaction is carried out on filterpaper. Nickel and iron give the same colour, only it is discoloured by 2N HCl.

NICKEL.

Bivalent, Kation $Ni^{..}$; moreover a hydroxide of trivalent nickel.

1. A l k a l i   h y d r o x i d e s give a green prec. of basic salts or $Ni(OH)_2$, insol. in an excess. An alkaline suspension of $Ni(OH)_2$ gives black $Ni(OH)_3$ when bromine water, not when H_2O_2 is added.

2. A m m o n i a first gives $Ni(OH)_2$ (provided not too much ammonium salts are present), easily sol. in an excess of NH_3, forming blue complex nickelo-ammonia kations, like $Cu^{..}$, only the colour is paler. An excess of KOH prec. $Ni(OH)_2$ again from this solution. KOH and bromine water gives a prec. of black $Ni(OH)_3$.

3. A m m o n i u m   s u l p h i d e gives a black prec. of NiS; hydrogen sulphide in dilute mineral acid solutions

does not. Nevertheless NiS, like CoS, once precipitated, is insol. in dilute HCl (1 : 10). NiS easily remains in colloidal solution (brown), which may be precipitated by boiling with dilute acetic acid.

DROP REACTION:

a. Nickel salts in dilute ammoniacal or Na-acetate solution give a red precipitate with dimethylglyoxime. (TSCHUGAEFF) [23])

> Cf. the reaction with $Fe^{..}$. When Co is present at the same time, it is advisable to turn the red colour of $Co^{..}$ into green cobaltitartrate complexes, in which the red Ni-precipitate is much more easily visible (FEIGL, priv. comm.).

b. Neutral nickel salts give a violet colour with dithiooxamide (rubeanic acid) (RÂY and RÂY) [23a])

> The reagent, $\begin{array}{c} S{=}C{-}NH_2 \\ | \\ S{=}C{-}NH_2 \end{array}$, is dissolved into ethyl alcohol.
> Very sensitive reaction, espec. when the stain on filter paper is developed over NH_3, but not specific! (Co, Cu etc.).

MANGANESE.

Bivalent, Kation $Mn^{..}$; moreover tetravalent in manganese peroxide and the manganites, hexavalent in MnO_4'', heptavalent in MnO_4'.

1. A l k a l i h y d r o x i d e s give a nearly white prec. of $Mn(OH)_2$, insol. in an excess; when kept in contact with air it is oxidised to MnO, MnO_2, aq, brown.

2. A m m o n i a gives no prec. at all, when enough amm. salts are present. When kept in contact with air, MnO, MnO_2, aq is prec. after some time. When Fe, Al, Cr etc. are present, manganites may be precipitated.

3. A m m o n i u m c a r b o n a t e gives a prec. of $MnCO_3$, also when amm. salts are present in excess (distinction from Mg).

4. A m m o n i u m s u l p h i d e gives a buff coloured prec. of MnS, easily sol. in dilute HCl. When boiled with amm. sulphide it obtains a greenish-grey hue.

5. When Mn-compounds, no matter which, are molten with soda and $NaNO_3$ (or even without $NaNO_3$) green sodium manganate is formed. Excellent and specific reaction.

6. When heated with strong oxidising agents, like PbO_2 and HNO_3, persulphate and H_2SO_4 (and $Ag^{\cdot}$ as a catalyst) or KIO_4 and dilute H_3PO_4, manganous compounds give a violet solution of $HMnO_4$. Specific.

DROP REACTIONS:

a. When $Mn(OH)_2$ is brought together with benzidine acetate both are readily oxidised in contact with air, causing the benzidine compound to turn into a bright blue colour. (FEIGL)[24])

> The reagent is $H_2NC_6H_4$—$C_6H_4NH_2$. It turns blue with all sorts of oxidising agents, so these must be absent. The reaction is very sensitive, but not specific. Cobalt and cerium give the same reaction. However, the Co-reaction is hindered by tartaric acid. Large amounts of chlorides interfere.

b. The oxidation with KIO_4 and dilute H_3PO_4 can be successfully employed as a drop reaction. (WILLARD and GREATHOUSE[25]). See chapter VI. It is specific, but somewhat capricious. Beware of too strong H_3PO_4.

ZINC.

Bivalent, Kation $Zn^{\cdot\cdot}$, anion ZnO_2''.

1. A l k a l i h y d r o x i d e s give a white prec. of $Zn(OH)_2$, easily sol. in an excess of the reagent. Amm. chloride does not reprecipitate the hydroxide from this solution (distinction from $Al^{\cdot\cdot\cdot}$). It can be reprecipitated by exact neutralization at $p_H = 8$—9.

2. A m m o n i a may give the same prec., but it is very easily sol. in an excess of ammonia, forming complex zinc-ammonia kations.

3. H y d r o g e n s u l p h i d e in extremely dilute mineral acid solutions (such as those containing sodium acetate) and a m m o n i u m s u l p h i d e give a white prec. of

ZnS, sol. in mineral acids, insol. in acetic acid (distinction from Mn).

4. P o t a s s i u m   f e r r o c y a n i d e gives a white prec., only slightly sol. in dilute mineral acids.

DROP REACTION:

a. By means of $(NH_4)_2Hg(CNS)_4$ in almost neutral solution. (BEHRENS)

> When carried out under the microscope, the typical white featherlike crystals of $ZnHg(CNS)_4$ may be observed. When carried out on the drop plate, it is advisable to add a trace of Cu·· in order to make the prec. better visible (MONTEQUI, see under Cu).

b. When a drop of a dithizone solution in CCl_4 (green, freshly prepared) is added to a *zincate*, the colour turns red. (FISCHER) [25a])

> A great many other metals react with dithizone, diphenyl-thiocarbazone, $S = C < \genfrac{}{}{0pt}{}{NH\text{-}NHC_6H_5}{N = NC_6H_5}$; Al does not; the reaction is specific for Zn, when Zn is isolated from the other $(NH_4)_2S$-metals by means of KOH.

BARIUM.

Bivalent, Kation Ba··.

1. A m m o n i u m   c a r b o n a t e gives a white prec. of $BaCO_3$, sol. in dilute and weak acids, even perceptibly in an excess of NH_4Cl.

2. A m m o n i u m   o x a l a t e gives a white prec. of $Ba(COO)_2$, provided the sol. is not too dilute. The prec. is sol. even in dilute acetic acid (distinction from Ca).

3. S u l p h a t e   i o n s give a white prec. of $BaSo_4$, even in very dilute solutions (distinction from Ca).

4. B a r i u m   c h l o r i d e and b a r i u m   n i t r a t e, when evaporated to dryness, are insoluble in HCl (1.19) resp. in HNO_3 (1.42, better 1.51). This is an excellent microchemical separation from Ca, not from Sr.

5. Both barium chloride and barium nitrate are insoluble in abs. ethyl alcohol (distinction from Sr and Ca).

6. P o t a s s i u m   b i c h r o m a t e gives a yellow prec. of

$BaCrO_4$. When the solution contains free mineral acids, sodium acetate must be added. The prec. is sol. in dilute mineral acids, but insol. in acetic acid (distinction from Ca and Sr).

DROP REACTION:

A neutral solution of $Ba^{..}$-salts gives a red-brown prec. with sodium rhodizonate, insoluble in very dilute HCl. (FEIGL)[25b])

The reagent is $\begin{array}{l} OC\!-\!CO\!-\!C\!-\!ONa \\ \ |\qquad\quad \| \\ OC\!-\!CO\!-\!C\!-\!ONa \end{array}$. Its solution in water is not stable! Sr gives the same reaction, but the prec. is sol. in dilute HCl.

STRONTIUM.

Bivalent, Kation $Sr^{..}$.

1. A m m o n i u m   c a r b o n a t e gives a white prec. of $SrCO_3$, sol. in dilute and weak acids, even perceptibly in an excess of NH_4Cl.

2. A m m o n i u m   o x a l a t e gives a white prec. of $Sr(COO)_2$, sol. in dilute mineral acids and slightly in acetic acid.

3. S u l p h a t e   i o n s give a white prec. of $SrSO_4$, provided the solution is not too dilute. A saturated $CaSO_4$-solution can be used for this purpose (distinction from Ca.) Gentle heating.

4. S t r o n t i u m   n i t r a t e is insoluble in abs. ethyl alcohol, strontium chloride, provided it is not completely dehydrated, is sol. in abs. ethyl alcohol. It is practically insol. in HNO_3 1,4 (about 18 mgrs. in 100 cc. HNO_3). Calcium nitrate is easily sol.

5. A l k a l i   c h r o m a t e s give no prec. in exactly neutral aqueous strontium solutions. When however an equal volume of ethyl alcohol is added, $SrCrO_4$ is prec. It is advisable to heat slightly (to about 70°) in order to prevent prec. of K_2CrO_4.

With sodium rhodizonate: see Ba. The best Sr-reactions are the microchemical reactions as $Sr(NO_3)_2$ and as $SrCrO_4$.

CALCIUM.

Bivalent, Kation Ca¨.

1. A m m o n i u m   c a r b o n a t e gives a white prec. of $CaCO_3$, sol. in dilute and weak acids, even perceptibly in an excess of NH_4Cl. Gentle heating is advisable in order to prevent the formation of soluble calcium bicarbonate or carbamate.

2. A m m o n i u m   o x a l a t e gives a white prec. of $Ca(COO)_2$, sol. in dilute mineral acids, insol. in acetic acid.

3. S u l p h a t e   i o n s only give a prec. in very conc. solutions. When the sol. is partly evaporated, $CaSO_4$, 2aq will separate as needles, which can be identified under the microscope. Avoid an excess of mineral acid. Very good reaction.

4. Both calcium nitrate and calcium chloride are easily sol. in abs. ethyl alcohol.

5. A l k a l i   c h r o m a t e s never give a prec.

6. P o t a s s i u m   f e r r o c y a n i d e and some solid NH_4Cl gives in neutral or feebly ammoniacal solutions a white prec. of calcium-ammonium ferrocyanide (distinction from Sr and Ba, not from Mg). Oxidising agents, such as chromates, must be absent, because they will oxidise the ferrocyanide ion.

MAGNESIUM.

Bivalent, Kation Mg¨.

1. A l k a l i   h y d r o x i d e s and b a r y t a water give a white prec. of $Mg(OH)_2$, but only when ammonium

salts are absent. With ammonia the prec. is incomplete even in this case.

2. A m m o n i u m   c a r b o n a t e   gives an incomplete white prec. of $MgCO_3$, only when other ammonium salts are absent (distinction from Mn).

3. A m m o n i u m   p h o s p h a t e   gives a white prec. of $MgNH_4PO_4$, aq. also when other ammonium salts are present; the prec. is easily sol. in dilute acids.

4. O r t h o - o x y q u i n o l i n e (O x i n e) gives a complete prec. in dilute ammoniacal solution, also when a large excess of ammonium salts is present. Not selective at all!

5. When a suspension of $Mg(OH)_2$ in water, or one of the carbonate or of the phosphate in dilute KOH, is boiled with some drops of "T i t a n - y e l l o w", the precipitate is coloured a violet-red (KOLTHOFF) [26]) (distinction from Ca, Sr and Ba).

> The reagent, or the methyl homologue "Clayton-yellow", is a very complicate organic dye, and is also known as "azidine-yellow 5 G". I t   i s   n o t   a t   a l l   s e l e c t i v e, so it can be used only when Mg and the alkaline earths are present alone, like in our scheme. Ferric hydroxide interferes, so the reagents must be free from iron. The violet-red colour of the magnesium dye must not be confused with the orange-red colour of the alkaline dye. An excess of NH_4-salts hinders the reaction.

6. A similar reaction is given by p. nitrobenzene-azo-resorcinol. (WEISSELBERG) [26a])

> The reagent is dissolved in 2N KOH. It gives a blue dye with $Mg(OH)_2$, whereas the calcium compounds are not coloured at all.

POTASSIUM.

Monovalent, Kation K·.

1. Nearly all potassium salts are readily sol. in water. Exceptions are the perchlorate, the chloroplatinate, the bitartrate, the picrate, the silicofluoride, the uranate.

2. A freshly prepared solution of $Na_3Co(NO_2)_6$, neutral

or slightly acetic acid, gives a yellow crystalline prec., composition about $K_2NaCo(NO_2)_6$ (distinction from Na·, not from NH_4·). (DE KONINCK) [27])

> This reaction is carried out in the cold on a microscopic object glass. Traces of Mg, Ca, Sr and Ba do not interfere, but NH_4· gives the same reaction. The reagent is best stored as the solid salt and may be prepared according to the prescription of BIILMANN [28]).

3. Neutral potassium salts give a yellow prec. with a solution of dipicrylamine in sodium carbonate. (PoLUEKTOFF) [28a])

> The reagent is $NH(C_6H_2(NO_2)_3)_2$. The crystal form is very typical (rhombs). NH_4-salts give the same reaction, Mg-salts do not interfere.

4. Remember the microchemical potassium reaction with H_2PtCl_6 and with $HReO_4$.

SODIUM.

Monovalent, Kation Na·.

1. Nearly all sodium salts are readily sol. in water. Exceptions are $Na_2H_2Sb_2O_7$ and some Na-uranium compounds.

2. In a neutral or very slightly acetic acid solution a pale yellow prec. is brought about after some time by a solution of zincuranyl acetate (distinction from K· and NH_4·). (KOLTHOFF) [29])

> This reaction is carried out on an object glass. The crystalline prec. may be identified under the microscope. It is essential, that the solution of the reagent is prepared exactly as described by KOLTHOFF. The reaction is not very sensitive, so, if necessary, the sodium solution is concentrated in a porcelain dish. Too much contact with glass must be avoided, because this may bring sodium into the solution. A large excess of potassium interferes and is best removed by means of perchloric acid.

3. Remember the microchemical sodium reactions with uranyl acetate and with a clear, saturated solution of potassium hydropyro-antimonate.

AMMONIUM.

Monovalent, Kation $NH_4^.$.

1. Nearly all ammonium salts are readily sol. in water. Exceptions are the chloroplatinate, the bitartrate, the picrate, the uranate. The perchlorate and the silicofluoride are soluble (distinction from $K^.$).

2. When ignited at 200—400° C, all ammonium salts completely lose their NH_3.

3. When boiled with KOH or NaOH, gaseous NH_3 is given off, which may be identified by its smell and its reaction on a wet red litmuspaper.

   Cyanides also give NH_3 when boiled with KOH. Not however when $HgCl_2$ has been added beforehand.

4. An alkaline solution of K_2HgI_4 gives a reddish-brown colour or a prec. with ammonium salts. (NESSLER) Exceedingly sensitive reaction!

   The reagent is prepared by treating a $HgCl_2$-solution with no more KI than is necessary to redissolve the prec., and adding some KOH.

CHAPTER II.

ANIONS.

CHLORIDE, BROMIDE AND IODIDE.

Ions Cl', Br', I'.

1. S i l v e r n i t r a t e, in dilute nitric acid solution, gives prec. of AgCl, white, AgBr, a pale yellow, AgI, yellow. All these are sol. in KCN and in $Na_2S_2O_3$. AgCl is readily sol. in ammonia; AgBr is slightly sol.; AgI insol. in ammonia. All are reduced by means of Zn and H_2SO_4, bringing the halogen ion in solution. Only AgCl is decomposed by N/2 KOH.

2. C o n c. s u l p h u r i c a c i d oxidises HBr and HI, not HCl.

3. Strong oxidising agents give the free halogens, at least in an acid solution. HI is the easiest oxidable, e.g. by means of HNO_2 or ferric salts, HBr less easily, e.g. by means of PbO_2 and dilute acetic acid or chlorine water, HCl the least easily.

4. Free bromine changes the pale yellow colour of a fluorescein paper to red. (GANASSINI) [30])

   Very sensitive reaction and specific for bromine; chlorine and NO_2 do not show this reaction.

5. S o l i d p o t a s s i u m b i c h r o m a t e and conc. sulphuric acid transforms solid chlorides into brown fumes of volatile CrO_2Cl_2. Sensitive and specific when fluorides are absent. (FEIGL and KAPULITZAS)

   The fumes may be caught in a drop of water, in which they form chromic acid, which may be identified by means of diphenylcarbazide. Nitrates interfere with this reaction, but can be reduced to NH_4-salts.

FLUORIDE.

Ions F' or HF_2'.

1. S i l v e r n i t r a t e gives no precipitate.

2. B a r i u m c h l o r i d e gives a prec. only in neutral or alkaline solutions, easily sol. in dilute HCl.

3. Soluble fluorides and HF discolour a hydrochloric acid solution of zirconium-alizarin dye.

4. When gently heated in a lead or Pt-crucible with conc. sulphuric acid, most fluorides give off HF-fumes, which etch glass. When at the same time quartz is present, SiF_4 is evolved, which may be detected:

   a. by catching the fumes in a drop of dilute NaCl-solution on a cellon object glass and observing under the microscope the typical crystals of Na_2SiF_6. This is a specific and very sensitive reaction.

   b. by catching the fumes in a drop of water and showing the presence of dissolved silicic acid in the drop as described under the head "Silicate". (FEIGL)
   It is most advisable to use quartz powder and not amorphous silica, because the latter may give rise to the formation of $SiOF_2$, which is not volatile, instead of SiF_4. As some mineral complex fluorine products are not readily attacked by sulphuric acid, it is often necessary to decompose these substances by fusing them with solid NaOH on a nickel crucible lid. The product of fusion is then treated as above.

CYANIDE. (POISONOUS!)

Ion CN'.

1. S i l v e r   n i t r a t e, in dilute nitric acid solution, provided it is present in excess, gives a white prec. of AgCN, easily sol. in NH_3, in $Na_2S_2O_3$ and in KCN. When treated with dilute sulphuric acid 1 : 1 on a steam bath, it is completely decomposed.

2. C a r b o n i c   a c i d gas expells HCN, especially when some $NaHCO_3$ has been added to the luke warm solution (distinction from CNS', Cl' etc.).
   Collect the HCN in a drop of ammonium polysulphide, acidify the drop, expel H_2S and test for CNS' by $Fe^{\cdots}$.

3. H o t   c o n c.   s u l p h u r i c   a c i d decomposes all cyanides, incl. the complex cyanides.

4. F e r r o u s   h y d r o x i d e (far better than ferrous salts)

changes CN′ into Fe(CN)$_6$′′′′, which can be detected by adding HCl and FeCl$_3$.

5. S u l p h u r (and Na$_2$S$_2$O$_4$) transform cyanides into sulphocyanates, which can be detected by means of HCl and FeCl$_3$.

SULPHOCYANATE.

Ion CNS′.

1. S i l v e r n i t r a t e, in dilute nitric acid solution, gives a white prec. of AgCNS, easily sol. in NH$_3$, in Na$_2$S$_2$O$_3$ and in KCN. When treated with dilute sulphuric acid 1 : 1 on a steam bath, it is completely decomposed.

2. H o t c o n c. s u l p h u r i c a c i d decomposes all sulphocyanates.

3. H o t c o n c. n i t r i c. a c i d oxidises all sulphocyanates (incl. AgCNS) to sulphates.

4. F e r r i c s a l t s, in acid solution, give a bright red colour.

FERRO- AND FERRICYANIDE.

Ions Fe(CN)$_6$′′′′ and Fe(CN)$_6$′′′.

1. S i l v e r n i t r a t e, in dilute nitric acid solution, gives with Fe(CN)$_6$′′′′ a white prec., with Fe(CN)$_6$′′′ an orange prec.; only the latter is sol. in NH$_3$.

2. D i l u t e h o t s u l p h u r i c a c i d gives a very slow evolution of HCN.

3. C o n c. h o t s u l p h u r i c a c i d decomposes all complex cyanides, forming, among other products, CO, combustible with a blue flame, and amm. sulphate.

4. F e r r i c salts give with Fe(CN)$_6$′′′′, f e r r o u s salts with Fe(CN)$_6$′′′, both only in acid solutions, a blue colour or a precipitate, in both cases about KFeFe(CN)$_6$.

5. T h o r i u m n i t r a t e gives in a dilute mineral acid solution a white prec. with Fe(CN)$_6$′′′′, not with Fe(CN)$_6$′′′.

6. C a d m i u m s u l p h a t e gives in a dilute mineral

acid solution, a prec. with both (distinction from halides, CN′ and CNS′).

7. R e d u c i n g a g e n t s change $Fe(CN)_6′′′$ to $Fe(CN)_6′′′′$. O x i d i s i n g a g e n t s cause the reverse reaction.

SULPHATE.

Ion $SO_4′′$.

1. B a r i u m c h l o r i d e gives in a dilute mineral acid solution a white prec. of $BaSO_4$.

2. S i l v e r n i t r a t e gives a prec. only in very conc. solutions. Typical microsc. crystals of Ag_2SO_4.

3. A solution of m e r c u r i c n i t r a t e, prepared by treating crystals of mercuric nitrate with a very dilute HNO_3 (e.g. 1 %) and filtering, gives a yellow colour or a yellow prec. of 3 HgO. SO_3 with traces of sulphate (even $BaSO_4$ and $PbSO_4$). (DENIGÈS) [31]) (capricious reaction).

SULPHIDE.

Ion $S′′$, mostly $HS′$.

1. S i l v e r n i t r a t e gives in a dilute acid solution a black prec. of Ag_2S, decomposed by HNO_3 1 : 1.

2. D i l u t e a c i d s evolve H_2S from soluble and some insol. sulphides. H_2S may be detected by means of a wet Pb-acetate paper.

3. I o d i n e gives in dilute acid solutions a prec. of sulphur. In neutral solutions some sulphate is also formed.

4. S o d i u m n i t r o p r u s s i d e, $Na_2FeNO(CN)_5$, gives in a dilute ammoniacal solution a violet colour.

5. Solid and dissolved sulphides catalytically accelerate the otherwise very slow reaction of s o d i u m a z i d e (NaN_3) with i o d i n e. A lively evolution of nitrogen is observed. (FEIGL) [32])

> This sensitive reaction can also be studied with success under the microscope. It is not specific, as some other sulphur compounds, e.g. thiosulphates and thiocyanates have the same effect. Moreover some mineral sulphides, e.g. CuS, do not show the reaction.

SULPHITE.

Ion SO_3''.

1. Silver nitrate gives no prec. in dilute mineral acid solutions. In neutral solutions a prec. is obtained only when enough $Ag^.$ is added. When the solution or the prec. is boiled, Ag is separated.

2. Barium chloride gives no prec. in dilute mineral acid solutions. In contact with air, a prec. of $BaSO_4$ is soon formed.

3. Strontium chloride gives a prec. of $SrSO_3$ in neutral solutions (distinction from thiosulphate).

4. Dilute sulphuric acid gives an evolution of SO_2, espec. when heated, which can be identified by its smell and by its action on a KIO_3-starch paper.

5. Malachite green is discoloured by neutral sulphites (distinction from thiosulphate).

THIOSULPHATE.

Ion S_2O_3''.

1. Silver nitrate, provided it is present in excess, gives a white prec. of $Ag_2S_2O_3$, which is sol. in an excess of $Na_2S_2O_3$. It is easily decomposed when boiled, separating black Ag_2S.

2. Strontium chloride gives no prec. (distinction from sulphite).

3. Dilute sulphuric acid, and other acids, give, after some time, a separation of sulphur and evolution of SO_2.

4. Iodine in acid solutions gives tetrathionate, chlorine and bromine give sulphate.

5. Mercuric chloride gives in an exactly neutralized solution first white Hg_2SCl_2 etc., then black HgS. The liquid becomes strongly acid (distinction from sulphite).

NITRATE AND NITRITE.

Ions NO_3' and NO_2'.

1. P o t a s s i u m   i o d i d e in acid solution is oxidised by nitrites, not by nitrates.

   It should be borne in mind however, that nitric acid, if not quite freshly prepared from nitrate and dilute sulphuric acid, and all conc. nitric acid, always contains nitrous acid. On the other hand, all acid nitrite solutions always contain nitrate.

2. All normal nitrates and nearly all nitrites of inorganic bases are soluble in water. Silver nitrite is prec. from rather conc. solutions and that only in the cold.

3. D i p h e n y l a m i n e, dissolved in conc. sulphuric acid, gives a violet-blue colour with both nitrates and nitrites (and with a great many other oxidising agents).

4. F e r r o u s   s u l p h a t e is coloured brown by NO: that means, that it is coloured by nitrites even in dilute acid solutions; by nitrates only when these are first decomposed by conc. sulphuric acid (ring reaction).

5. N i t r i t e s in dilute acid solution form diazo compounds with aromatic amines, which can be condensed with other amines or phenols to form azo-dyes. For instance a mixture of α-naphthylamine and sulphanilic acid is a very good reagent for nitrites, giving a red colour. (ILOSVAY V. ILOSVA) [33]) Exceedingly sensitive reaction!

6. By the action of zinc and acetic acid nitrates can be reduced to nitrites, which may be detected als described above.

7. A sulphuric acid solution of $KMnO_4$ is discoloured by nitrites, not by nitrates.

CHLORATE.

Ion ClO_3'.

1. Especially in an acid medium, all chlorates are oxidising agents. All normal chlorates of inorganic bases are soluble in water.

2. Conc. sulphuric acid forms a yellow gas, ClO_2, which is *very* explosive and has a peculiar smell. Dangerous!

3. Hydrochloric acid is oxidised only slowly and after prolonged heated with chlorates, except when these are very conc. (distinction from hypochlorites).

4. Reducing agents, such as SO_2, change chlorates to chlorides, which can be detected by silver nitrate and nitric acid.

PERCHLORATE.

Ion ClO_4'.

1. Silver nitrate and barium chloride give no prec.

2. Solutions of perchlorates are only very difficultly reduced, e.g. not by Zn, SO_2 and HI. They can be reduced by $Mo^{...}$, i.e. molybdate and zinc in an acid solution.

3. When ignited at about 500° C, the alkali perchlorates are completely decomposed in chloride and O_2.

4. Potassium salts give a white crystalline prec., provided the solutions are not too dilute.

5. Methylene blue in neutral solutions of perchlorates gives a prec. of meth. blue perchlorate; violet needles; microscope; persulphates give the same reaction.

ORTHOPHOSPHATE.

Ions H_2PO_4', HPO_4'' and PO_4'''.

1. The normal, tertiary phosphates are insol. in water (except K, Na and NH_4). $AlPO_4$ and $FePO_4$ are insol. in dilute acetic acid, $BiPO_4$ and $ZrOHPO_4$ are even insol. in dilute mineral acids (max. 0.30 N). Ferric iron interferes with the prec. of $BiPO_4$. A great many primary and secundary phosphates are sol. in water.

2. Together with metastannic acid (or tin and conc. nitric acid), phosphoric acid forms a complex phospho-

metastannic acid, insol. in nitric acid, perceptibly sol. in dilute HCl.

3. A m m o n i u m m o l y b d a t e and HNO_3 produce a yellow crystalline prec., composition about $(NH_4)_3PO_4$, 12 MoO_3, 2 HNO_3, H_2O, easily sol. in NH_3. When only traces of phosphate are present, the precipitation takes some time. Gentle heating is advisable. A yellow colour alone is no sufficient indication of phosphates, as it may be caused by dissolved SiO_2. Arsenates give the same reaction, only it takes a longer time. When kept cold, no prec. is obtained in any reasonable time.

4. S i l v e r n i t r a t e gives a yellow prec., only in neutral, not in acid or ammoniacal solutions (distinction from meta- and pyrophosphates, which give white prec.).

5. All phosphorus compounds, when heated with m a g n e-s i u m powder in a closed tube, give Mg_3P_2, which can be detected by bringing it into some water or very dilute HCl: evolution of PH_3; smell.

   The phosphorus compound and the magnesium powder must be completely dehydrated beforehand. When water is left in the mixture, d a n g e r o u s explosions may occur.

6. Phospho-molybdic acid is reduced by benzidine acetate, which gives a blue solution.

   The reaction must be carried out in an about neutral solution, so sodium acetate is added. Oxalic acid prevents the reaction, tartaric acid does not (distinction from silicic acid and arsenic acid, which do not form complexes with molybdic acid when tartaric acid is present. Cf. silicate").

CARBONATE.

Ions CO_3'' and HCO_3'.

1. All normal carbonates, except those of K, Na and NH_4, are insoluble in water. A great many bicarbonates are soluble.

2. D i l u t e a c i d s give an evolution of carbonic acid gas, which renders a drop of $Ca(OH)_2$ turbid. A more sensitive reaction for the detection of CO_2 gas is its

effect on a drop of Na_2CO_3, coloured by some phenol-phthalein. This solution is discoloured. (FEIGL and KRUMHOLZ) [34])

> In order to prevent a discoloration by SO_2, it is advisable to use chromic acid for the decomposition of the carbonate. Some mineral carbonates, e.g. $MgCO_3$, yield CO_2 only after prolonged boiling.

SILICATE.

Perhaps no ions at all. Hypothetical SiO_3'', SiO_4'''' etc.

1. H y d r o c h l o r i c a c i d gives silicic acid, insol. in water, but always remaining for the greater part in colloidal solution. Only by (twice) evaporating to complete dryness and heating, it is changed to a product, which is insol. in dilute mineral acids. A great many mineral silicates are not attacked at all by HCl, especially the complex aluminosilicates. These must first be decomposed by fusion with solid NaOH on a nickel plate or in a nickel crucible.

2. The only really specific reaction of silicates is their behaviour towards HF (KF and H_2SO_4). SiF_4 is volatilised (distinction from all other oxides. TiO_2 is slightly volatile with HF alone, not with HF and H_2SO_4). SiF_4 can be caught in a drop of water (on a cellon plate) which is rendered turbid by the separation of gelatinous SiO_2, aq. The dissolved (colloidal) SiO_2, aq can be identified by means of the next reaction. Avoid an excess of HF.

3. Dissolved (colloidal) SiO_2, aq reacts with hot ammonium molybdate and HNO_3, giving an intensively yellow solution of silico-molybdic acid. Tartaric acid prevents this reaction, oxalic acid does not (distinction from phosphoric acid). Silico-molybdic acid is more easily reduced than molybdic acid, e.g. by benzidine acetate. When this reagent and an excess of solid sodium acetate is added, a blue solution is obtained.

Very sensitive reaction. (FEIGL and KRUMHOLZ) [35])
Nitrates and iodides interfere with this reaction.

> The blue colour is due to a blue $Mo^{...}$- or Mo^V-compound
> and a blue oxidation product of benzidine. The reaction is
> considerably hindered by the presence of Cl′-ions, so these
> are better avoided. It is so sensitive, that it must be
> carried out in a test tube of really resistive glass or, better,
> in a small porcelain crucible. In order to make the reaction
> specific, it is advisable to separate the SiO_2, beforehand
> by means of KF and H_2SO_4. CaF_2 often contains traces
> of SiO_2, so we prefer the use of KF.

BORATE.

Ions BO_3''', BO_2', B_4O_7''.

1. When a drop of borate and dilute HCl is brought on
   a turmeric paper (i.e. paper soaked in curcumin, dis-
   solved in alcohol) and the paper is dried by gentle
   heating, a reddish-brown stain is obtained. Conc. HCl,
   $Fe^{...}$, Ti, Zr, Cu, Ni and some other products give the
   same reaction, but when the stain is treated with a drop
   of dilute KOH, only the boric acid stain is changed to
   dark green.

2. Boron compounds are volatilised by treating the free
   boric acid (which is considerably volatile on itself with
   steam) with HF (i.e. a mixture of CaF_2 and $KHSO_4$ in
   the loop of a platinum wire) or with methyl alcohol.
   BF_3 and $B(OCH_3)_3$ can be detected by passing them in
   a colourless flame (green colour). When carefully
   carried out, this is a specific and very sensitive reaction.

3. Boric acid alone does not discharge the red colour of
   phenolphthalein. The addition of (neutral) glycerol is
   necessary. Have the solution containing the indicator
   just alkaline and no more.

ORGANIC ANIONS.

Systematic analysis of organic anions is a subject apart,
far beyond the scope of this manual. We must content

ourselves with giving some reactions of the most important ones: formates, acetates, oxalates and tartrates.

1. The majority of organic anions are charred, when heated in a small test tube. Formates, oxalates and some acetates (K, Na, NH₄, Ca, Sr, Ba, Mg) show no charring, provided enough water of crystallisation or free acid is present.

2. Formic acid and acetic acid are volatile. They are distilled off, when their salts are treated with dilute H_2SO_4 1 : 2. The distillate is substantially acid (smell, taste, indicators).

3. Formic acid is a strong reducing agent (e.g. on $HgCl_2$, which, in not too strongly acid solution, is changed to Hg_2Cl_2) (distinction from acetic acid).

4. Oxalates and formates, when treated with conc. sulphuric acid, give an evolution of CO.

5. Oxalates give a prec. with $CaCl_2$, insol. in acetic acid. Tartrates also give a prec., insol. only in very dilute acetic acid. The prec. of calcium tartrate, once washed out with water, and very gently heated with a suspension of AgOH in dilute NH_3 (dilute silver nitrate with NH_3, not quite enough to redissolve the prec. of AgOH) produces a silver mirror on the test tube (distinction from oxalates).

6. Oxalates, when molten together with diphenylamine and taken up in alcohol give a blue solution (aniline blue, FEIGL and FREHDEN [37])

7. Dry alkali acetates, when heated in a small tube with finely powdered As_2O_3, produce the typical smell of the very toxic gas cacodyl oxide.

8. Acetates, when heated with conc. sulphuric acid and ethyl alcohol, produce the typical smell of ethyl acetate (fruity odour).

9. Tartaric acid and tartrates in dilute acetic acid solution give a white crystalline prec. with a conc. solution of potassium salts.

CHAPTER III.

THE LESS GENERAL ELEMENTS. *)

The possible presence of the following elements is to be dealt with:
a. in the HCl-group: Tl and W.
b. in the H_2S-group: W, Mo, Au, Pt, V, Cb, Ta, Se and Te.
c. in the NH_3-group: Ce, Th, La, Nd, Y, Er, Ti, Zr and Be.
d. in the $(NH_4)_2S$-group: Tl.
e. in the alkaline earth group: Li.
f. in the alkali group: Li, Rb and Cs.

A c o m p l e t e s e p a r a t i o n w h e n a l l t h e s e e l e m e n t s
a r e p r e s e n t, i f p o s s i b l e a t a l l, i s c e r t a i n l y f a r b e y o n d
t h e s c o p e o f t h i s m a n u a l and hardly of any real use, because
the case never presents itself in practice. We must content ourselves
with the problems when and where to find evidence of them and
how to identify them in that case. Instead of a "rigid" system we
will use "incidental" procedures. In the summary given below we will
restrict ourselves to such reactions as are really typical and more
or less selective. The best means of detection and identification are
given in small type in Chapter V, the systematic course.

THALLIUM.

Monovalent (thallous) and trivalent (thallic) kations.

1. The thallous compounds resemble the alkali salts in many
   respects. In other respects they are like the silver salts. TlOH is
   a strong soluble base. The thallic salts are easily hydrolysed
   because $Tl(OH)_3$ is a very weak base.

2. Thallous chloride is only slightly soluble in cold water, readily
   in hot water (like $PbCl_2$). The bromide and iodide are even less
   soluble. All are not soluble in NH_3 (distinction from Ag˙).

3. Oxidants like H_2O_2 or Br_2 give in alkaline solutions of thallous
   salts a brown precipitate of $Tl(OH)_3$, insoluble in an excess
   of KOH or NH_3.

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*) The term "rare" elements is quite out of place for some of them, which
are not "rare" at all: e.g. Ti, Be, Zr, Ce, Mo, W and others. Only they give
us a lot of trouble in analytical work and are therefore, often deceptively,
kept in the background.

4. Thallous sulphide, brown, is, like ZnS, not precipitated by H_2S from a strongly acid solution, but it is practically insoluble in dilute acetic acid.

5. By far the best identification of thallium compounds is by means of their typical green flame colour.

6. Towards KI and K_2CrO_4 thallous salts behave like lead salts, but TlI is only sparingly sol. in hot water.

TUNGSTEN (WOLFRAMIUM) AND MOLYBDENUM.

Both normally hexavalent in anions WO_4'' and MoO_4'', colourless.

1. Both H_2WO_4 and H_2MoO_4 are insoluble in water, but H_2MoO_4 is easily soluble in an excess of acid, whereas H_2WO_4 *) is not. Both oxides WO_3 and MoO_3 are soluble in alkali; when the oxides have been ignited, it may be necessary to fuse with NaOH.

2. A solution of MoO_3 in HCl, as well as a suspension of WO_3 in HCl is reduced by metallic Zn or Sn to a lively blue solution containing probably trivalent W and Mo. In the long run, especially in the case of Mo, the reduction proceeds further to brown products. Niobium also gives a blue reduction product when treated with Zn in an acid solution, but its colour is more a dull greyish-blue.

3. Hydrogen sulphide in acid solution may give brown precipitates of MoS_3 and WS_3, but, especially in the case of W, the precipitation is very easily retarded. In this way both Mo and W can remain undetected until the carbonate group! Both MoS_3 and WS_3 are easily soluble in KOH and in alkali sulphides, giving rise to the formation of alkali sulphomolybdates and -tungstates. Addition of HCl then precipitates the sulphides. Moreover, especially in the case of Mo, hydrogen sulphide has a distinctly reducing action on the hexavalent compounds.

4. A trace of solid molybdate, boiled with some drops of conc. H_2SO_4 in a small test tube, cooled and treated with some drops of alcohol gives a blue coloration. W does not give this reaction.

5. An hydrochloric acid solution of Mo, treated first with some KCNS, then with a drop of $SnCl_2$, gives a red coloration. This is a very sensitive reaction, which is not shown by W-compounds. The red colour of $Fe(CNS)_3$ may be prevented by the addition of tartaric acid.

6. A tungstate heated on a porcelain dish with solid $NaHSO_4$ and

*) H_2WO_4 can dissolve in cold conc. HCl, but is prec. on boiling.

a drop of conc. H_2SO_4, and cooled, gives a red coloration, when treated with solid phenol. Mo-compounds do not show this reaction.

7. Hydrogen peroxide gives a yellow colour in acid solutions of Mo, a reddish colour in ammoniacal solutions. The reaction is not very sensitive and therefore hardly interferes with the detection of Ti and V by means of H_2O_2.

8. A solution of $(NH_4)_2MoO_4$ in conc. HNO_3 gives the well known yellow crystalline precipitate with phosphates. Remember, that the presence of $NH_4^{\cdot}$-ions is essential.

GOLD.

Monovalent (aurous) and trivalent (auric) kations, of which the trivalent are by far the most important. Moreover a great many complex anions, like $AuCl_4'$.

1. The aurous compounds are characterized by insoluble halides, like $AuCl$.

2. Aurichydroxide is precipitated only from conc. solutions and easily soluble in an excess of alkali hydroxide, forming aurates.

3. NH_3 in not too dilute auric solutions gives rise to the formation of a yellow precipitate of "fulminating gold".

4. Hydrogen sulphide gives brown to black Au_2S_3, mixed with free gold. Therefore the precipitate is only partially soluble in $(NH_4)_2S$ and practically insol. in KOH. Insoluble in HCl 1 : 1.

5. Both $FeSO_4$, H_2SO_3 and oxalic acid in acid solution reduce the auric salts to a brown precipitate of gold (distinction from Pt). In an alkaline solution a great many more reducing agents (like HCOH etc.) reduce to metallic gold, giving rise to violet-blue colloidal solutions: very sensitive reaction.

PLATINUM.

Bivalent (platinous) and tetravalent (platinic) kations, of which the tetravalent are by far the most important. Moreover a great many complex anions, like $PtCl_6''$.

1. In conc. solutions, NaOH gives a yellow prec. of $Pt(OH)_4$, soluble in an excess of the reagent, forming platinates. Slightly soluble in NH_3.

2. Hydrogen sulphide gives a dark brown prec. of PtS_2, mixed with Pt, insoluble in HCl 1 : 1, partially soluble in $(NH_4)_2S$ and practically insoluble in KOH. (Note: the residue also contains the whole of the other Pt-metals Ru, Rh, Pd and Os; iridium sulphide is, like PtS_2, partially soluble in $(NH_4)_2S$).

3. Only very strongly reducing agents (Zn etc.) reduce platinum solutions in an acid medium. $FeSO_4$, H_2SO_3 and oxalic acid do not (distinction from Au). In alkaline solution Pt is precipitated by a great many reducing agents.

4. Alkali iodide gives a dark redbrown colour, probably caused by PtI_4''-ions. Very sensitive reaction.

5. Finely divided Pt, such as formed by heating K_2PtCl_6 on an asbestos fibre, may be brought to glowing, when held in a stream of gas and air. Very sensitive reaction.

6. When evaporated with KCl, a Pt-solution is changed into K_2PtCl_6, yellow octahedrons (microscope), sparingly soluble in water, insoluble in ethyl alcohol.

VANADIUM.

2-, 3-, 4- and pentavalent kations. More important is the anion VO_3'.

1. Conc. solutions give a redbrown prec. of V_2O_5 when H_2SO_4 is added, soluble in an excess of acid and by dilution. HCl is less useful, because it is oxidised by vanadates to Cl_2 (KI-starch-paper).

2. Reducing agents like $SnCl_2$, SO_2, oxalic acid (and even H_2S) give blue solutions, which contain $V_2O_2^{....}$, divanadyl (derived from tetravalent V). Alkali iodides give green solutions, containing $V^{...}$, vanadic. Metals like Zn and Al in acid solution finally give greyish-violet $V^{..}$, (vanadous), via blue and green.

3. Hydrogen sulphide gives a brown prec. of V_2S_5 only from conc. solutions. Dilute solutions of vanadates are reduced to blue divanadyl compounds. Ammonium sulphide gives no precipitate, but at once a violet-red solution, probably containing a sulphosalt of divanadyl. This is about the best means of detection of V. When acidified, these solutions yield brown V_2S_5.

4. Hydrogen peroxide and H_2SO_4 gives a red solution of pervanadic acid (HVO_4). This solution is not discoloured by F'ions (distinction from Ti). The red colour cannot be extracted by means of ether. An excess of peroxide must be avoided.

COLUMBIUM AND TANTALUM.

Pentavalent; most important are the anions CbO_3', TaO_3' and more complex anions. Both the alkaline and the acid solutions of Cb and Ta are very easily hydrolysed, giving prec. of Cb_2O_5, aq and Ta_2O_5, aq, which, when once boiled, are only sparingly

soluble in acids or KOH. Sodium columbate and tantalate are only sparingly sol. in dilute NaOH; the potassium salts are far more soluble in KOH. Acid columbium solutions are reduced by zinc, giving a grey or greyish-blue colour; tantalum solutions remain colourless. A hydrochloric acid solution of Cb gives an orange-red colour with tannin; Ta turns pale yellow (Ti orange-red, W chocolate brown). The detection of these elements, though very important for some groups of mineral products, is hardly possible along ordinary analytical lines. The best way is the micro-chemical identification as $Na_8Cb_6O_{19}$ and K_2TaF_7. (See chapter on "residue insoluble in aqua regia"). In the microcosmic bead Cb with a trace of $Fe^{..}$ gives a blue colour (distinction from Ta). A complex fluoride solution of Ta is decomposed when boiled: blue prec. Cb-solutions do not show this reaction.

SELENIUM.

Tetravalent; Kation $Se^{....}$, more important the anion SeO_3''. The anion SeO_4'', in which Se is hexavalent, is rather unstable.

1. Hydrogen sulphide gives a bright yellow prec. of SeS_2, soluble in KOH and in $(NH_4)_2S$, decomposed (separation of S and Se) by HCl 1 : 1. When precipitated from boiling solutions, it is red, probably a mixture of S and Se.

2. Reducing agents like H_2SO_3, KI, $SnCl_2$ etc. in an acid medium (about HCl 1 : 1) give a bright red prec. of Se. This is a good way to remove selenious compounds from others of the same group.

3. Codeïne, dissolved in conc. H_2SO_4, gives a green colour. Very sensitive.

4. Selenium compounds give the hepar reaction like S-compounds.

5. Selenium compounds are easily detected by their bright blue flame colour, by the typical, very disagreeable smell when heated (like garlic) and by the red deposit from most of its fumes on a cold porcelain dish.

TELLURIUM.

In all respects like Se. The TeO_4''-ions are even more unstable. The prec. with H_2S is brown. Contrary to Se, tellurium is not prec. from a strongly acid solution (HCl 1 : 1) by H_2SO_3. $FeSO_4$ does not prec. it at all (other distinction from Se).

When a moist prec. of tellurium is treated on the drop plate

with a very small bit of metallic sodium (1 mm³ will do!), a violet colour is produced.

When metallic tellurium is treated with some drops of hot conc. sulphuric acid on a porcelain dish, a red solution is obtained (selenium gives a greenish colour).

CERIUM.

Trivalent, Ce$\cdots$, cerous and tetravalent, C$\cdots$, ceric. The cerous salts are colourless (when pure, free from Nd), the ceric salts are orange.

Cerous salts:

1. KOH and NH₃ give a gelatinous, white prec. of Ce(OH)₃, insoluble in an excess of the reagents. Very slightly soluble in an excess of cold (NH₄)₂CO₃-solution. In contact with air, the alkaline suspension is slowly turned into ceric hydroxide.
2. Oxalic acid and amm. oxalate give a white prec., insoluble in dilute mineral acids (group reaction) and insoluble in an excess of amm. oxalate (distinction from Th, Y and Zr).
3. Neither sodium acetate nor sodium thiosulphate give prec. (distinction from Al and from Th).
4. Potassium iodate gives a prec. in neutral solutions, Ce(IO₃)₃, 2aq, soluble in mineral acids.
5. Hydrogen peroxide gives no prec. in neutral or acid solutions. In alkaline suspensions, Ce(OH)₄, orange, is formed: very specific reaction. Same with bromine and KOH.
6. Hydrofluoric acid gives a white prec. of CeF₃.H₂O, slightly soluble in an excess of HF.
7. When evaporated to dryness with some KOH and taken up in strychnine and conc. H₂SO₄, a bluish-violet colour is formed, which turns red after some time.

Ceric salts:

1. Reducing agents (and H₂O₂) turn the orange coloured ceric salts into colourless cerous salts, especially in an acid medium.
2. Sodium salicylate gives a brown colour.
3. Because ceric hydroxide oxidises a solution of benzidine acetate, cerous salts give the same reaction as Mn$\cdot\cdot$ in this respect.

THORIUM.

Only colourless tetravalent kations Th$\cdots$.

1. KOH and NH₃ give a gelatinous, white prec. of Th(OH)₄, insoluble in an excess of the reagents.

2. $(NH_4)_2CO_3$ gives a similar prec., soluble in an excess of the cold reagent.

3. Oxalic acid and amm. oxalate give a white prec., insoluble in dilute mineral acids, soluble in an excess of amm. oxalate. When boiled, it remains dissolved (like Zr, unlike Y), but when HCl is added, it is prec. again (unlike Zr).

4. Sodium acetate and thiosulphate give a white precipitate, especially when boiled (distinction from Ce).

5. Potassium iodate gives a white prec. of $Th(IO_3)_4$, only very sparingly soluble in even conc. HNO_3, especially when an excess of KIO_3 is present.

6. Hydrogen peroxide gives a white prec. in very slightly acid solutions. Thorium sulphate reacts immediately, the chloride and the nitrate only after some time. Boiling with some drops of dilute H_2SO_4 accelerates the precipitation.

7. Hydrofluoric acid gives a white prec. of ThF_4, 4 aq, insol. in cold water (distinction from Al, Be, Zr, Ti).

8. The best way for the detection of small amounts of Th is the extraction with a slightly ammoniacal $(NH_4)_2CO_3$-solution and then making use of the excellent microchemical reaction by means of solid thallous nitrate: very specific yellow rhombs of thorium-thallous-ammonium-carbonate.

LANTHANUM, NEODYMIUM, YTTRIUM, ERBIUM, etc.

The "rare earths" in a narrower sense.

Practically only trivalent kations $La^{...}$, $Nd^{...}$, $Y^{...}$, $Er^{...}$ etc. The lanthanum salts are colourless, the neodymium salts rose, the yttrium salts colourless and the erbium salts pale rose.

1. Oxalic acid and amm. oxalate (group reagent.) give a prec., insoluble in dilute mineral acids (0,3N). Yttrium oxalate is somewhat soluble in an excess of hot amm. oxalate solution, from which it is prec. on cooling.

2. Amm. carbonate gives precipitates, all more or less (espec. with Er and Y) soluble in an excess of the cold reagent.

3. Alkali hydroxides and NH_3 give a prec., insoluble in an excess.

4. Hydrofluoric acid gives a prec., insoluble in an excess of HF, more or less resistant to dilute mineral acids, especially with La, only slightly with Y.

5. Neodymium and Erbium are best detected by means of their absorption spectra; Yttrium by the fact, that its double salt

with K_2SO_4 is soluble in a cold saturated K_2SO_4-solution, whereas the corresponding compounds of La, Er and Ce are insoluble.

6. Lanthanum may be detected by the reaction of its basic acetate with iodine vapours: intensive blue colour, like starch with iodine. For procedure see chapter "Systematic course".

TITANIUM.

Tetravalent: Kation $Ti^{····}$, anion TiO_3'', both colourless; less important trivalent kation $Ti^{···}$ violet.

1. Both dilute acid and dilute alkaline solutions are very easily hydrolysed when boiled. The precipitate, meta-titanic acid, is only sparingly soluble in acids and alkali hydroxides. This is the best way to remove Ti (together with Cb and Ta): boil for some hours in $1/2\%$ HCl.

2. Cold KOH, NaOH and NH_3 give prec. of titanic acid, soluble in an excess of cold KOH, insoluble in NH_3 but considerably in cold $(NH_4)_2CO_3$ (distinction from Al).

3. Hydrogen peroxide gives in a sulphuric acid solution of $Ti^{····}$ an orange colour, caused by TiO_2, H_2O_2, aq. Very sensitive reaction. Vanadium gives the same reaction, only with Ti the colour disappears when NaF is added (by the formation of very stable TiF_6''-ions).

4. Zinc and tin reduce an acid solution to violet $Ti^{···}$-compounds.

5. TiF_4 is not volatile in the presence of sulphuric acid (distinction from Si).

6. Cupferron (NH_4-salt of nitrosophenylhydroxylamine) gives a prec. from acid solutions (distinction from Al and Be).

7. Chromotropic acid gives in a not too strongly acid solution a reddish-brown to violet colour. Freshly prec. TiO_2, aq, also gives the reaction. Sensitive and specific. $UO_2^{··}$ and $Fe^{···}$ give a similar reaction, but can be reduced by means of $SnCl_2$.

ZIRCONIUM.

Tetravalent: Kations $Zr^{····}$ and especially $ZrO^{··}$ (zirconyl); anions ZrO_3'' etc.

1. ZrO_2, aq is more pronouncedly a basic oxide than TiO_2. Therefore the acid solutions are far more stable than the corresponding Ti-solutions. The alkaline solutions are very unstable.

2. KOH, NaOH and NH_3 give a white prec. of zirconium hydroxide,

easily soluble in dilute HCl when prec. cold, not when hot (insol. in hot 0,3 N HCl). It is hardly soluble in an excess of KOH. Na_2ZrO_3 is practically insoluble in water (as with Cb and Ta), especially when NaOH is present (distinction from Ti and Si). The basic carbonate is readily soluble in cold $(NH_4)_2CO_3$ (distinction from Al).

3. Oxalic acid and amm. oxalate give a white prec., soluble in an excess of amm. oxalate. Zirconium sulphate does not show this reaction, because in this salt the greater part of the Zr is present in the form of $ZrO(SO_4)_2''$-anions.

4. Zirconium phosphate is practically insoluble even in 0,3 N HCl.

5. Hydrofluoric acid gives no precipitate (distinction from rare earths).

6. An acid (1 N HCl) solution of $ZrO^{..}$ is coloured violet by alizarin-S (gentle heating) by the formation of a very stable zirconium-alizarin mordant dye. Sulphate ions considerably hamper this reaction (see sub 3). Fluorine ions completely discolour the dye by the formation of very stable ZrF_6''-ions.

BERYLLIUM (GLUCINUM).

Bivalent, colourless kations $Be^{..}$.

1. Alkali hydroxides and NH_3 give a white prec. of $Be(OH)_2$, only slightly soluble in an excess of NH_3, readily soluble in an excess of cold KOH (when not boiled) from which solution the $Be(OH)_2$ may be partially reprecipitated by boiling (like $Cr^{...}$).

2. Ammonium carbonate gives a white prec. of $BeCO_3$, soluble in an excess of the reagent (distinction from Al). When boiled for some time, the $(NH_4)_2CO_3$ is decomposed and $BeCO_3$ is reprecipitated.

3. Oxalic acid and amm. oxalate do not give a prec. (distinction from Ce, La etc.).

4. Ortho-oxyquinoline (oxine) in an acetic acid solution containing amm. acetate gives no precipitate (distinction from Al).

5. Quinalizarin gives a bright blue colour to feebly alkaline (0,2 N KOH) $Be^{..}$-solutions. Mg gives about the same reaction.

6. One of the best reactions of Be is the microchemical precipitation with potassium oxalate: large, highly refractive and highly birefringent monoclinic crystals.

LITHIUM.

Monovalent, colourless kations Li˙.

1. The properties of the lithium compounds are often intermediates between those of calcium and those of sodium compounds. Li_2CO_3, Li_3PO_4 and LiF are only sparingly soluble in water. On the other hand they are not so insoluble as to resist the action of solutions of low pH, like NH_4Cl, in which they are readily soluble. All three can only be precipitated from solutions, which contain a large excess of OH', such as caused by NaOH or KOH, not always by NH_3.

2. Hydrochloropatinic acid and sodium cobaltinitrite give no prec. (distinction from K etc.).

3. Lithium chloride is readily soluble in a mixture of equal volumes of ethyl alcohol and ether, whereas NaCl and the other alkali chlorides are practically insoluble. This is the only reliable separation from Na.

4. Lithium compounds show a bright red flame colour, like Sr. The difference may be seen by means of a simple hand spectroscope.

RUBIDIUM and CAESIUM.

Monovalent, colourless kations Rb˙ and Cs˙.
The properties of rubidium and caesium compounds are very similar to those of potassium salts. The differences are only gradual. The chloroplatinates and cobaltinitrite compounds are less soluble, the bitartrates more soluble than the corresponding potassium salts. The more striking differences are:

1. Cs_2CO_3 is insoluble in absolute ethyl alcohol, whereas Rb_2CO_3 and K_2CO_3 are perceptibly dissolved.

2. When the chlorides are evaporated to dryness on a microscopic object glass, both RbCl and CsCl give a precipitate with a drop of a H_2SnCl_6-solution, whereas KCl does not. When treated with a drop of a H_2SbCl_5-solution, only CsCl gives a precipitate. However it is essential that the H_2SnCl_6-and the H_2SbCl_5-solutions should be prepared according to recipe. (See chapter "Systematic course").

3. When solid CsCl is brought into contact with a drop of a solution of AgI in conc. KI and a drop of ethyl alcohol (do not dilute with water) a white crystalline prec. is formed, consisting of needles (distinction from Rb, which gives a granular prec. or no prec. at all). (GRAVESTEIN) [30])

4. Both Rb and Cs give a violet flame colour, very much like K. By means of a good spectroscope the different spectrum lines may be identified.

OTHER ELEMENTS.

There are a great many other elements, some of them not even so very rare, which may be encountered in the analysis of mineral products, e.g. the rarer elements of the Pt-group (ruthenium, Ru, rhodium, Rh, palladium, Pd, osmium, Os, and iridium, Ir), germanium, Ge, related to Sn, with a volatile chloride and a frequent constituent of spelter, indium, In, with a typical blue flame colour, gallium, Ga, scandium, Sc, etc. etc. For all these elements we refer to the handbooks, especially those of spectroscopic practice.

CHAPTER IV.

DRY WAY ANALYSIS; PRELIMINARY TESTS.

A great many useful indications can be gathered in this way in a short time. Moreover the procedures of dry way analysis are often an essential part of mineralogical research and of geological field work. At the same time they have a great didactical value, because they teach us how to obtain results with a minimum of apparatus.

fig. 1   fig. 2
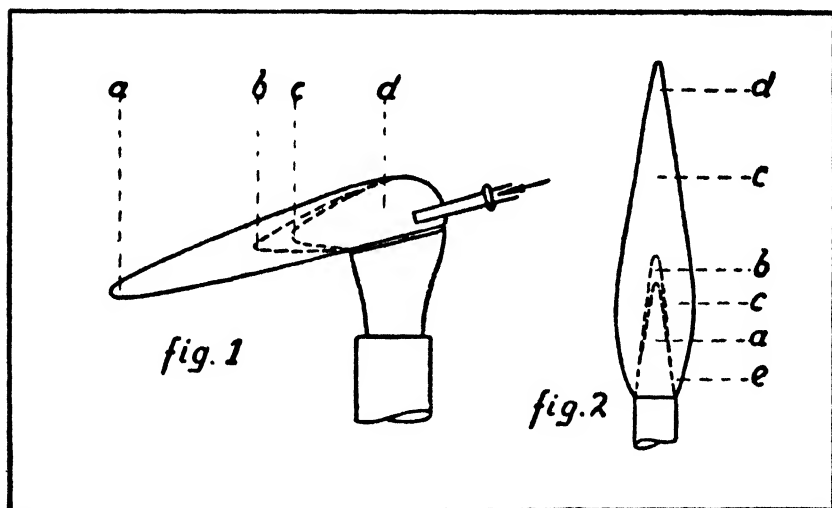
The most important parts of dry way analysis are b l o w-p i p e   a n a l y s i s,   f l a m e   c o l o u r s,   b e a d   c o l o u r s   and h e a t i n g   i n   a   c l o s e d,   n a r r o w   t u b e. The b l o w p i p e f l a m e is represented in fig. 1. Like a Bunsen flame it has, besides a luminous part d, which contains incandescent carbon particles, an inner core b-c, in which carbon monoxide is present and an outer zone till a. It is evident, that the parts from d to b, and especially at c, are reducing zones; the best part for oxidation purposes is at a; the place of maximum

temperature is somewhat to the right of *a*. The student should learn to maintain an u n i n t e r r u p t e d stream of air for at least two minutes.

The B u n s e n f l a m e is represented in fig. 2. The cold mixture of gas and air, which is present at *a*, does not contain enough air for complete combustion to CO_2 and H_2O. In the inner core *b* it is transformed into a mixture of CO, CO_2, H_2 and H_2O. So it is evident, that *b* is the appropriate place for reduction purposes. This mixture (water gas) is gradually oxidised by outside air to CO_2 and H_2O in the outer zone. The best oxidising part is at *d*. The hottest parts are at *c*. The part *e* at the base is rather cold and suitable for flame colour tests.

Bead tests and flame colour tests can be carried out both in the Bunsen flame and in the blowpipe flame.

I. BLOWPIPE ANALYSIS ON CHARCOAL.

The finely powdered substance is mixed with about twice its volume of anhydrous sodium carbonate, brought into a small pit on the surface of the charcoal and heated in the reducing blowpipe flame.

We may obtain: m e t a l l i c g l o b u l e s or a magnetic mass, and o x i d e c o a t i n g s at some distance from the assay. This depends on the possibility of reducing the oxides of the metals present by means of charcoal, the fusion point and the volatility of the metals: see table I. When there is evidence of globules, which will not grow, it is advisable to repeat the operation with potassium oxalate or potassium cyanide as a flux in stead of sodium carbonate (silver, tin).

T A B L E I.

A. M e t a l l i c m a s s, n o t m o l t e n; m a g n e t i c:
Nickel, cobalt and iron.

B. G l o b u l e s, n o o x i d e c o a t i n g; the globules are malleable.
Silver, copper and gold.

C. Globules and an oxide coating.

Bismuth: globule not malleable; coating brownish yellow to greenish white.

Antimony: globule not malleable; coating white to bluish; volatile.

Tin: globule malleable; coating white, only slightly volatile.

Lead: globule malleable, writes on paper; coating yellow.

D. No globules, only an oxide coating.

Arsenic: white, very volatile; smell.

Cadmium: nearly black to brown and yellow (peacock's feather).

Zinc: yellow when hot, white when cold.

The globules obtained are treated with nitric acid and investigated by appropriate reactions.

The operation is repeated for the detection of s u l p h u r c o m p o u n d s, but this time with a candle flame (because town gas always contains traces of sulphur). All sulphur compounds (incl. sulphates), when mixed with sodium carbonate and ignited on charcoal, give sodium sulphide, which may be detected by bringing the reaction product with a drop of water on a bright silver coin. Black deposit. (H e p a r r e - a c t i o n).

II. BEAD TEST.

This test can be carried out with borax or with microcosmic salt. The colour differences are not very striking, so we will restrict ourselves to the *borax beads*. They are prepared, once in the oxidising and once in the reducing flame and both times observed when hot and when cold. Always use a clean platinum wire; first prepare a small bead of pure borax; then add a small amount of the unknown substance. Sulphurous ores must first be roasted.

The typical colours are collected in table II.

TABLE II. Borax beads.

Substance	Oxidising flame		Reducing flame		Sensitive or not
	hot	cold	hot	cold	
Gold	rose-violet	rose-violet	red	violet	+
Molybdenum	pale yellow	colourless	brown	brown	— —
Tungsten	pale yellow	colourless	yellow	yellow-brown	— —
Vanadium	yellow	yellow-green	dirty green	green	++
Silver	yellow	opalescent	grey	grey	—
Copper	green	blue	colourless	opaque red	+
Bismuth	pale yellow	colourless	grey	grey	—
Antimony	pale yellow	colourless	grey	grey	—
Titanium	pale yellow	colourless	grey	violet	— —
Uranium	orange-yellow	pale yellow	pale green	pale green	—
Iron	orange-yellow	pale yellow	green	green	+
Chromium	yellow	yellow-green	green	green	— —
Cobalt	blue	blue	blue	blue	++
Nickel	violet	red-brown	grey	grey	+
Manganese	violet	brown-violet	colourless	colourless	++

+ means sensitive, — not sensitive.

III. FLAME COLOUR TEST.

The unknown substance is dissolved in a drop of conc. HCl and brought at the base of a colourless Bunsen flame at the end of a clean platinum wire. Substances, which are insol. in HCl, are prepared in such a way as to improve solubility; sulphurous ores are roasted, silicates are decomposed by

NaOH, the sulphates of barium and strontium are reduced to sulphides on charcoal or even in a luminous Bunsen flame, etc. etc.

The typical flame colours are collected in table III.

TABLE III. Flame colours.

Substance	Colour	Substance	Colour
Sodium	yellow	thallium	bright green
Potassium	pale violet	copper (oxid. comp.)	emerald green
Rubidium	pale violet	phosphoric acid	pale yellow-green
Caesium	pale violet	nitric acid	bronze green
Lithium	crimson red	zinc metal	pale bluish green
Strontium	crimson red	copper chloride	azure blue
Calcium fluoride	bright red	copper bromide	azure blue
Calcium	brick red	lead	pale azure blue
Barium	yellow-green	selenium	bright blue
Molybdenum	yellow-green	arsenic	pale bluish grey
Tellurium	pale green	antimony	pale bluish grey
Boron	bright green	bismuth	pale bluish grey

IV. HEATING IN A CLOSED TUBE.

A. Without sodium carbonate.

The substance is heated first gently, at last in the hottest part of a Bunsen burner in a narrow and small glass tube. We may observe: changes of colour, sublimates, evolution of gases and vapours.

1. The possible changes in colour are of such a diversity, that it is hardly possible to describe them all.

SnO_2, ZnO, ZnS, Sb_2O_3 and TiO_2 are yellow, when hot, white when cold. Organic matter is charred and turns brown or black. Smell. Copper, nickel, cobalt, manganese, uranium, silver and iron salts turn brown or black by the formation of oxides. Bismuth and cadmium oxide are more orange-brown, lead oxide is yellow.

2. S u b l i m a t e s:

W h i t e: ammonium salts, As_2O_3, Sb_2O_3, chorides of Al, Zn, Cd, Hg, Sn, Pb.
y e l l o w: S, As_2S_3, HgI_2 (red when cold), PbI_2, $NiCl_2$. ($FeCl_3$ brown).
r e d: $CrCl_3$, Sb_2S_3; violet-red: I_2, $CuCl_2$; b l u e $CoCl_2$.
b l a c k: Se, HgS, Hg (drops), As, Cd.

3. G a s e s a n d v a p o u r s: I : c o l o u r l e s s.

a. O x y g e n, detected by a glowing match:
nitrates, nitrites, chlorates, iodates, bromates, perchlorates, periodates, persalts, chromates, peroxides, etc. Ammonium nitrate gives N_2O.

b. C a r b o n d i o x i d e, detected by a drop of $Ca(OH)_2$; beware of SO_2. Carbonates, organic matter, oxalates. C a r b o n m o n o x i d e (blue flame) from oxalates and formates.

c. A m m o n i a, detected by a red litmus paper; smell. Ammonium salts, cyanogen compounds, organic N-bases.

d. S u l p h u r d i o x i d e, detected by smell and a KIO_3-starch-paper:
sulphides by oxidation, sulphites of heavy metals, some sulphates.

e. H y d r o g e n s u l p h i d e, detected by smell and a Pb-acetate-paper:
sulphides with water, thiosulphates.

f. HCl from hydrated chlorides, $(CN)_2$ and H C N from cyanogen compounds (ferricyanides), CS_2 and

$(CN)_2$ from sulphocyanates, SiF_4 from silico-fluorides, a c e t i c   a c i d from acetates.

4. G a s e s   a n d   v a p o u r s :   I I :   c o l o u r e d.
   a. NO_2 from nitrates and nitrites.
   b. Br_2 from bromium compounds. NO_2 and Br_2 have about the same colour; they can be distinguished by the fact, that Br_2 produces a reddish violet stain on a fluorescein-paper (chlorine and NO_2 do not).
   c. C h l o r i n e ,   i o d i n e ,   s u l p h u r ,   a r s e n i c.

B. M i x e d   w i t h   s o d i u m   c a r b o n a t e.
Specially note the evolution of NH_3 and the formation of metallic mirrors of arsenic (smell) and mercury (drops).
With the residue the h e p a r   r e a c t i o n is once more carried out. It now shows the presence of sulphur compounds except sulphates. *) Selenium and tellurium compounds give the same reaction, iodides interfere.
When the product of fusion is slightly green, repeat with sodium carbonate and $NaNO_3$ (manganese).

V.   HEATING IN A BENT OPEN TUBE.
This operation (roasting) is carried out in a tube represented by a very wide V. The material is placed in the bend and there it is gently heated. Roasting is advisable only for substances with a metallic appearance (metals, ores etc.).
Note the evolution of S and SO_2, sublimates of As_2O_3 (smell, octahedrons), SeO_2 (black and red seam, smell), TeO_2 (white, melts to a colourless liquid), Sb_2O_3 (also white or pale yellow, infusible), Hg (drops).

VI.   TREATING WITH SULPHURIC ACID.
This test is carried out with solid substances only. When the unknown is a solution, it is first evaporated to dryness.

A. With d i l u t e H_2SO_4. Gentle heating.
Note the evolution of gases:

---

*) Some sulphites do not show this reaction.

1. CO_2 from carbonates and cyanates (and so from cyanides).
2. O_2 from peroxides and persalts.
3. SO_2 from sulphites and thiosulphates.
4. H_2S, HCN, C_2H_2, a c e t i c acid, f o r m i c acid.
5. NO_2 from nitrites only.
6. Br_2, I_2, Cl_2 (from halides and oxidising agents).

B. With c o n c. H_2SO_4. Gentle heating.
1. HCl from chlorides, HBr and Br_2 from bromides, HI and I_2 from iodides.
2. HF from fluorides. SiF_4, when at the same time silicates are present. Etching of glass. SiF_4 makes a drop of water turbid.
3. SO_2 from heavy metals, sulphur, sulphides, carbon and organic matter; also from Hg_2Cl_2.
4. SO_2 and S from sulphocyanates and thiosulphates.
5. CO and CO_2 from a great many organic acids. Charring?
6. ClO_2 from chlorates. Very explosive; exceedingly dangerous.
7. Brown: Br_2 and HBr, NO_2 (now also from nitrates) and CrO_2Cl_2.
8. Violet: I_2 and HI, but also Mn_2O_7 from permanganates. Very explosive and exceedingly dangerous.

VII. REDUCTION WITH ZINC AND HCl.
Treat some drops of the solution (or suspension) in fairly strong HCl (about 1 : 1) with a small granule of zinc. Changes of colour:
colourless to blue (later green and brown): molybdenum and tungsten. The latter is turned brown only after a long time. Columbium gives a similar reaction.
yellow to green, later greyish: vanadium.
yellow to green: chromium.
colourless to violet: titanium.
yellow to pale green: iron.

CHAPTER V.

SYSTEMATIC COURSE.

[A.] OUTLINED SCHEME OF SEPARATIONS.

A. **A d d H C l** to the hot solution; $Hg_2^{\cdot\cdot}$ and $Ag^{\cdot}$ are prec.; separate with NH_3. A prec., when the liquid is cooled down, may be $PbCl_2$ and/or $TlCl$.
When Se and Te are present, they are removed by reduction.

B. **P a s s i n H $_2$ S**; extract the prec. with hot 2N KOH.
   a. **F i l t r a t e :** As, Sb and Sn (possibly also Hg). Detected separately.
        Mo.
   b. **R e s i d u e :** Hg, Cu, Bi, Pb, Cd.
        Au, Pt.

   Extract with hot HNO_3 1 : 1: residue HgS   (and Au and Pt); filtrate Cu, Bi, Pb and Cd. Divide it into two parts:
      1. **O n e p a r t** is treated with NH_3. Test the solution for Cu, the prec. for Bi and Pb. When Bi is present, Pb must be isolated as $PbSO_4$.
      2. **T h e o t h e r p a r t** is treated with KOH. The prec. is tested for Cd.

C. **A d d N H $_4$ C l a n d N H $_3$**; heat gently; U, Al, Fe and Cr are prec. (possibly also Mn)
        Also Ce, Th, La etc., Ti, Zr, Be.

   The prec. is extracted with hot amm. carbonate: U is dissolved (also part of Be). The residue is extracted with hot 2N KOH:

   a. **s o l u t i o n :** Al (and part of Be and Ti).
   b. **r e s i d u e :** Fe, Cr and Mn. (and Ti, Zr, Ce, Th, La etc.).

D. P a s s i n H₂S¹); Co, Ni, Mn and Zn (and rest of Tl) are prec. Dissolve in HCl and H₂O₂ and test for Co, Ni and Mn.

Isolate Zn by boiling with conc. NaOH (and event. H₂O₂).
The filtrate of this group may contain Mo and V.

The filtrate from D lends itself to two methods of treatment. No. I is the easier, but it is not very accurate, while No. II, though it entails more work, is very reliable.

I. E₁ Add NH₃ and a m m. c a r b o n a t e, heat gently and centrifuge:

F₁ The r e s i d u e contains the carbonates of Ca, Sr, Ba.

G₁ The s o l u t i o n is tested for Mg, K and Na.

II. E₂ Evaporate to dryness with o x a l i c a c i d, ignite to dull red; then evaporate with a m m. c a r b o n a t e and remove the amm. salts. Extract with water.

F₂ a. r e s i d u e: Mg, Ca, Sr, Ba. Divide into two parts:
1. one part is tested for Mg.
2. the other part is tested for Ca, Sr and Ba.

G₂ b. s o l u t i o n: K and Na (and Rb, Cs and Li).

H. The original substance is tested for NH₄˙.

[B.] PRELIMINARY OPERATIONS.

I. The dry analysis is carried out with the original substance. It consists of:

a. Heating with and without sodium carbonate in a small test tube. Note the evolution of vapours etc., charring, sublimates; hepar reaction.

b. Blowpipe analysis on charcoal.

c. Borax beads in oxidising and reducing flame.

d. Flame colour.

e. Treating with dil. and conc. sulphuric acid.

---

¹) Passing in H₂S has a distinct advantage over adding (NH₄)₂S, because the latter is seldom free from sulphates and so removes Ba and Sr from the solution.

II. **Preparing the sample for systematic analysis** consists of:

a. Test for SiO_2 and F. If present, SiO_2 is removed by evaporating to dryness with HCl; F is removed by boiling with conc. H_2SO_4.

> It should be borne in mind, that this operation may result in dissolving a great many substances, which otherwise would have remained insoluble in aqua regia: Cb, Ta, Ti, Zr compounds etc., and in the formation of insoluble sulphates.

b. Boiling for some time with sodium carbonate solution. The solution is tested for:

1. c o m p l e x   c y a n i d e s by acidifying and testing with a ferrous-ferric-solution. They are removed by boiling with conc. H_2SO_4.

2. o x a l a t e s (with acetic acid and $CaCl_2$). When $Fe(CN)_6''''$ and/or F' are present, they also give a prec. Ferrocyanides may be removed by H_2O_2; if F' is present, the prec. is filtered or centrif. off and tested for oxalates by means of dil. H_2SO_4 and $KMnO_4$.

   Oxalates are removed by igniting to a dull red heat. When volatile metals are present at the same time, the oxalates are better destroyed by evaporating (till SO_3-fumes are given off) with HNO_3 (2 : 1) and 4N H_2SO_4.

c. Bringing the substance into solution:

1. Extract with water; test with litmus and add dil. HNO_3 by drops and note the formation and the character of a prec.

   > W, Ti, Zr, Cb and Ta are prec. here. When a prec. is formed, the best procedure is to evaporate with aqua regia and taking up in hot dil. HCl. A residue is treated as sub V: insoluble substances. The solution is treated in the ordinary systematic way. Remember, that now Ag is removed at the same time!

2. Extract with dil. and conc. HCl.

3. Evaporate to dryness with aqua regia, then extract with hot dil. HCl.

The systematic analysis is carried out with a solution, which contains no, or at least only small amounts of nitric acid!

[C.] KATIONS.

A. When no HCl has been employed for dissolving the substance, it is now added to the hot solution. AgCl and Hg_2Cl_2 are prec. Lead is washed out with hot water; the residue is treated with NH_3. A black colour shows Hg_2Cl_2; the prec. is centrifuged off, the solution is slightly acidified with dil. HCl. A prec. is AgCl. It is identified by centrifuging off and testing with manganous hydroxide.

> If a prec. is formed when the filtrate is cooling, this may be $PbCl_2$ or TlCl. The presence of Tl may be proved by the flame colour, separating from Pb by means of dil. H_2SO_4 and identifying with KOH and bromine water. If Tl was present, it is removed for the greater part by complete cooling of the solution. Traces escape and are found in the $(NH_4)_2S$-group.
>
> When the preliminary tests have shown the presence of Se and Te, these are now removed by reducing with SO_2, first in HCl 1 : 1 (Se), then in 2N HCl (Te). Se is identified by means of codeine and conc. H_2SO_4, Te by conc. H_2SO_4 alone or by reaction with metallic sodium.

B. The filtrate of the HCl-group is oxidised with bromine water (no large excess), the excess removed by boiling, and the acidity brought to about 2N HCl. Hydrogen sulphide is then passed into or over the hot solution. After 5 min. the acidity is reduced to about 0,2N HCl by diluting the liquid and controlling with a methyl violet paper. H_2S is then once more passed for 15 minutes into or over the solution.

> A blue colour of the solution may point to V or Mo. Both are found for the greater part in the filtrate of the $(NH_4)_2S$-group but vanadates may also be found in the NH_3-group.

A prec. is filtered off, washed with a very dil. NH_4NO_3 solution and transferred to a centrifuge tube, where it is treated with hot 2N KOH and centrifuged.

T h e   s o l u t i o n   contains $As^{...}$, $Sb^{...}$, $Sn^{....}$, and occasionally $Hg^{..}$ [1]) (and perhaps part of the M o).

Verify whether anything has been dissolved into KOH by acidifying a small portion with dilute HCl and shaking with benzene. Some drops of the solution are tested for As by alkaline reduction with Al and testing with $HgCl_2$.

To the greater part of the solution *only slightly* more than an equal volume of conc. HCl is added and gently heated (no boiling). A permanent, yellow[1]) prec. is As_2S_3 and is removed. The clear solution is boiled for some time to remove all H_2S. A big drop is tested for Sb by oxidation with $NaNO_2$ and testing with rhodamine-B; a greater part is reduced by Al-shavings, filtered off and tested for Sn with cacotheline.

> Some molybdenum may have been prec. by H_2S. In that case it has been dissolved in KOH and for the greater part reprecipitated by conc. HCl. Traces remain in solution and interfere with the detection of tin. So therefore, when Mo is present, the detection of Sn is better carried out by removing the greater part of HCl by prolonged boiling and testing for Sn with some drops of $HgCl_2$ (no excess): white or grey prec.

T h e   r e s i d u e   of the KOH extraction contains H g S, P b S, C u S, C d S and B i$_2$S$_3$ (and A u and P t, partly as sulphides, partly reduced to the metallic state). It is treated with hot HNO_3 1 : 1 and centrifuged.

T h e   s o l u t i o n   contains Pb, Cu, Cd and Bi. It is divided into two parts:

O n e   p a r t   is treated with an excess of NH_3; a blue colour indicates Cu. It is identified by acidifying with H_2SO_4 and

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[1]) Under circumstances, which have not been sufficiently cleared, HgS can dissolve in 2 N KOH when As, Sb and especially Sn are present. In that case, the prec., obtained by acidifying the alkaline extract is not yellow, but brown or even black. HgS is then separated from As_2S_3 by treating with NH_3 and identified as described later on. It does not interfere with the reactions on As, Sb and Sn.

testing with Zn·· and amm. mercuric sulphocyanate.

A precipitate indicates Pb and Bi. It is centrifuged off and tested for bismuth with Pb·· and K_2SnO_2. When Bi is present, the rest of the prec. is treated with some very dil. H_2SO_4 in a centrifuge tube, twice washed out with water. A residue points to Pb; it is identified by testing with tetramethyldiaminodiphenylmethane.

A n o t h e r p a r t is treated with an excess of KOH. A prec. is centrifuged off and tested for Cd by means of the Cd-mirror in a small test tube. Wash out the nitrates!

HgS (and A u and P t) remains behind undiss. in HNO_3 1 : 1; it is identified by dissolving in bromine water (or HCl and H_2O_2) and testing with diphenylcarbazide. When Cu is present, the identification of Hg·· is better carried out by means of $SnCl_2$ and aniline.

> When A u and P t are present, the residue (in HNO_3 1 : 1) is dissolved in aqua regia, the excess removed by careful evaporation; Pt is detected microchemically as K_2PtCl_6, Au with oxalic acid and Hg by means of metallic copper, not with diphenylcarbazide or with $SnCl_2$.

C. The filtrate of the H_2S-group is boiled for some time to remove all H_2S and part of the water. A small sample is then tested for phosphoric acid by means of amm. molybdate and some HNO_3. If phosphates are present, they may be removed in one of the following ways:

1. Evaporate to complete dryness with metallic tin and conc. HNO_3, once more evaporate with HNO_3 and take up the residue in dil. HNO_3. A great many metals are absorbed to a large extent.

2. A better, but more expensive procedure: boil down the filtrate of the H_2S-group to 50 ml., add 1 gr. of solid NH_4Cl and (for every 100 mgr. PO_4''') 5 ml. of a 10 % $ZrOCl_2$-solution and heat to boiling. Then add some drops of methyl-red and a very slight excess of NH_3. Boil for some minutes; then neutralise exactly with HCl and add 10 ml. of a 2N HCl. Boil again for some minutes. Centrifuge or filter the hot solution,

which now contains only traces of Zr. These will be found together with Fe and Cr and do not interfere with the retection of these elements.

The solution, free from phosphates, is now treated with some bromine water, the excess of bromine expelled by boiling. A gram of NH_4Cl and an excess of conc. NH_3 are added and the mixture heated to boiling and the flame removed. Avoid boiling the material. A prec. may contain A l, C r (not quite complete), F e, U and possibly Mn. [1]   (Also C e, T h, L a etc., T i, Z r and B e Perhaps also vanadates of iron etc.).

The prec. is centrifuged off and extracted with a *hot* solution of amm. carbonate; U is dissolved, separated in the centrifuge and identified by boiling with an excess of HCl and testing cold with ferrocyanide.

The residue of the carbonate extraction is treated with an excess of *hot* 2N KOH and centrifuged. When the solution is coloured brown by colloidal iron hydroxide, this is removed by prolonged boiling.

T h e s o l u t i o n contains Al. Identify by neutralising with HCl, using thymol blue (pH = 8,5) as an indicator. $Al(OH)_3$ is prec. (pure white). It is dissolved in dil. H_2SO_4 and identified by means of the alizarin-S reaction, or as Cs-Al-sulphate when Zr has been used for the elimination of phosphates.

T h e r e s i d u e of the KOH-extraction contains Cr, Fe and Mn. The presence of Fe is shown by means of HCl and KCNS, the presence of Cr by bromine, H_2SO_4, phenol and diphenylcarbazide, the presence of Mn by converting it into permanganate.

> C e, T h, L a etc., T i, Z r and B e are also prec. in this group. Moreover the prec. of V as brown divanadyl hydroxide or as some vanadate is possible. In order to prevent the prec. of alkaline earths etc. as vanadates, it is advisable to add some ferric salts. In that case only

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[1] Mn is prec. for the greater part here, when Al, Cr, Fe or U are present; not when it is present alone.

ferric vanadate is precipitated.

It is also advisable to test a small portion of the prec. at once for Ti by means of H_2SO_4 and H_2O_2 or by chromotropic acid and $SnCl_2$.

a. When treating with amm. carbonate, the boiling must be continued for some minutes. Otherwise nearly all of these elements will more or less go into solution. Be, Y and Er and traces of Th, Zr, Ti and Ce will remain in solution in any case. They do not interfere with the detection of U. The solution may be tested for Be by removing CO_2 with HCl, and adding an excess of KOH. U is precipitated. Be remains in solution and may be identified with quinalizarin or microchemically as acetyl acetonate. Y and Er may be separated from U by way of the oxalates and identified by means of the spectroscope.

b. When treating with hot 2N KOH it is also advisable to boil for some minutes. Aluminium, together with some Ti, Be and V are dissolved. It is not necessary once more to test for Ti and Be; however the Al reaction with alizarin-S is useless now. The surest way for the detection of Al besides Ti and Be (and a great many other elements) is the microchemical reaction as Al-Cs-alum.

c. The residue of the KOH-extraction contains Be, Zr, Ti, Ce, Th, La etc. besides Fe, Cr and traces of Mn. The residue is boiled for some minutes with 5 % oxalic acid and centrifuged hot (to prevent prec. of Zr):

1. T h e s o l u t i o n contains Fe, Cr, Zr, Ti and traces of Mn and Be. It is decomposed by evaporating with conc. H_2SO_4, excess expelled, taken up in water and prec. with NH_3. The prec. is tested for:
   F e with HCl and NH_4CNS.
   C r with KOH, Br etc.
   Mn with H_3PO_4 and KIO_4.
   T i as described above.
   Z r with alizarin-S in 1 N HCl.

2. T h e r e s i d u e contains Ce, Th, La etc. It is also decomposed by evaporating with conc. H_2SO_4, the excess of H_2SO_4 expelled, prec. again by NH_3, once more centrifuged and tested for:

C e by means of H_2O_2 and KOH and with benzidine acetate.

T h by extracting the prec. with a cold conc. solution of amm. carbonate and some NH₃ and testing the extract with a small grain of TlNO₃ under the microscope: swarm of typical yellow rhombs.

L a by the iodine reaction: La(OH)₃ is thoroughly washed out in the centrifuge, dissolved in some drops of dil. acetic acid by gentle heating, cooled down, prec. again by some drops of NH₃, separated and twice washed in the centrifuge. The prec. is transferred to an object glass and brought over some solid iodine: bright blue colour.

Y, E r etc. spectroscopically or microchemically.

D. H₂S is now passed for 10 min. on the hot, ammoniacal filtrate of the NH₃-group. N i, C o, M n, Z n and small amounts of C r are prec. and centrifuged off. The residue is dissolved in some conc. HCl (and H₂O₂ if necessary). The greater part of the acid is removed by evaporation and taking up in a little water. The solution is tested for:

C o with ethyl alcohol and NH₄CNS.

M n with KOH and benzidine acetate (if Co is present, it is necessary to add some tartaric acid) or with H₃PO₄ and KIO₄.

N i with dimethylglyoxime.

Z n by boiling for 3 minutes with an excess of 30 % NaOH (and some H₂O₂ if Co is present), centrifuging and neutralising the solution exactly with HCl and thymol blue (pH = 8,5). A prec. is Zn(OH)₂. It is once washed out in the centrifuge, taken up in some drops of dil. H₂SO₄ and tested for Zn by adding a trace of Cu·· and ammonium mercuric sulphocyanate, or by means of dithizone.

If no Cr has been found in the NH₃ group and the colour of the solution points to Cr, it is advisable to test here for Cr as described above.

If T l was present, it has not been completely removed as TlCl and the remainder will prec. in this group as Tl₂S. It may be detected once more by the flame colour. As Tl···-compounds interfere with the detection of Mn, and Tl·-salts do not, it is advisable, in that case, to use

no H_2O_2 for dissolving the sulphides, or, if the use of H_2O_2 is unavoidable, to reduce it afterwards by SO_2.

The filtrate of this group will contain the greater part of V and M o. A violet-red colour points to V, a reddish brown colour (provided polysulphides are present) to Mo. As the first operation in the next group is acidifying with acetic acid, both are precipitated there — after prolonged boiling — as sulphides, V_2S_5 and MoS_3, both brown. V may also give a blue divanadyl compound. Mo is detected by dissolving in conc. HNO_3, evaporating, taking up in HCl and testing with Zn or with KCNS and $SnCl_2$. V is detected by evaporating with conc. HNO_3 and testing with H_2O_2.

E. The filtrate of the $(NH_4)_2S$-group is acidified with acetic acid and boiled for some time to remove all H_2S. A prec. may be NiS (or MoS_3 or V_2S_5, see above). It is filtered off. If Mn was present, it may be necessary to remove the last traces of this element by adding NH_3 and H_2O_2.

The remainder of the separation may be conducted by following either of the given schemes:

I, an expedient way, permissible when small amounts of Ca, Sr and Ba may be neglected, or
II, more laborious, but suitable for the detection of minute amounts of the alkaline earths.

Method I:

E_1 NH_3 is added to the purified filtrate of the $(NH_4)_2S$-group until slightly alkaline reaction, if necessary NH_4Cl, and then $(NH_4)_2CO_3$. Heat gently for about 5 min., avoid boiling. Ca, Sr and Ba are prec. as carbonates. They are centrifuged off and treated according to F_1. The filtrate may contain Mg, K and Na. It is treated as sub G_1.

F_1 The carbonates are dissolved into as little dil. acetic acid as possible and CO_2 expelled. A small portion is tested for B a with $K_2Cr_2O_7$ and sodium acetate. If a yellow prec. is obtained, then the whole is treated in this way. $BaCrO_4$ is separated in the centrifuge. The solution is treated hot

with solid Na_2CO_3 to prec. Sr and Ca as carbonates. They are centrifuged off, washed and evaporated to dryness in a small crucible with HNO_3. After cooling, the nitrates are taken up in a small volume of HNO_3 (sp. gr. 1,4) and centrifuged. A residue is $Sr(NO_3)_2$. It is identified microchemically as nitrate and as chromate, and by means of the flame colour. When Ca was present, it has been dissolved by HNO_3 1,4. The solution is evaporated to dryness, taken up in water and C a detected microchemically as $CaSO_4$, 2 aq and by means of solid NH_4Cl and a solution of $K_4Fe(CN)_6$.

G, The filtrate of the carbonate precipitation is divided into two unequal parts:

a. *The smaller part* is tested for M g by adding amm. phosphate and boiling. A prec. shows Mg. As however traces of Ca etc. may prec. here just as well as phosphates, it is essential to confirm the presence of Mg by centrifuging off, taking up in dilute KOH and boiling with some drops of titan yellow.

b. *The greater part* is tested for K and Na. It is evaporated to dryness and ignited in a porcelain dish to remove all NH_4-salts. The residue is taken up in water and centrifuged. The solution is divided into two parts:

1. One part is tested for K by means of a freshly prepared solution of $Na_3Co(NO_2)_6$.

2. The other part is tested for N a by means of a suitable solution of zinc-uranyl acetate.

Method II:

E, A small portion of the purified filtrate of the $(NH_4)_2S$-group is first tested for the presence of sulphates[1]). If these are present (and consequently no Ba and only traces of Sr), they are removed in a slightly acidified solution with a small excess of $BaCl_2$.

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[1]) Because these will be only very incompletely transformed into carbonates during the subsequent treatment with oxalic acid etc.

The solution is now evaporated in a small porcelain dish and the ammonium salts expelled. Then some (pure) solid oxalic acid is added and ignited till a dull red heat, (under the hood). After cooling, some mls. of a (pure) amm. carbonate solution are added and once more ignited till *all* ammonium salts have been completely expelled, but at no higher temperature than necessary. After cooling, some water is added, transferred to a centrifuge tube and centrifuged. A residue is treated as sub F_2, the solution as sub G_2. Note the last paragraph of F_2.

F_2 The residue is dissolved into as little dil. acetic acid as possible, and CO_2 expelled by boiling. If necessary separated from impurities in the centrifuge and divided into two unequal parts:

a. *The smaller part* is tested for M g by adding KOH, which has been freed beforehand from carbonates by means of some drops of $BaCl_2$. A prec. may be Mg $(OH)_2$. Mg is identified by boiling the suspension of the prec. in KOH with some drops of titan yellow.

b. *The greater part* is tested for Ca, Sr and Ba. A small portion is tested for Ba with $K_2Cr_2O_7$ and sodium acetate. If a yellow prec. is obtained, then the whole is treated in this way. $BaCrO_4$ is separated in the centrifuge. The solution is treated with a small excess of solid Na_2CO_3, boiled and centrifuged. The carbonates of Sr and Ca are washed with water and evaporated to dryness in a small crucible with HNO_3. After cooling, the nitrates are taken up in a small volume of HNO_3 (sp. gr. 1,4) and centrifuged. A residue is $Sr(NO_3)_2$. It is identified microchemically as nitrate and as chromate and by means of the flame colour. If Ca is present, it has been dissolved by HNO_3 1,4. The solution is evaporated to dryness, taken up in water and C a detected microchemically as $CaSO_4$, 2 aq and by means of solid NH_4Cl and a solution of K_4 Fe $(CN)_6$.

When very large amounts of Mg are present, small amounts of Ca can only be detected by isolating them beforehand as Ca-oxalate.

It must be borne in mind, that when sulphates were present in the $(NH_4)_2S$-filtrate, and consequently no Ba, the whole treatment sub F_2 is only intended for the purpose of detecting Ca and at most traces of Sr. The separation by means of HNO_3 may then be omitted.

> Traces of Li may also remain undissolved as Li_2CO_3 in this group. It is best detected by means of the spectroscope and does not interfere with the detection of Mg, Ba, Sr and Ca.

G_2 The aqueous extract of the carbonates may contain K and Na (and Li, Rb and Cs) and traces of Mg and the alkaline earths, which do not interfere with the detection of K and Na. The solution is divided into two equal parts: One part is tested for K. The solution is once more evaporated and gently ignited to remove all traces of amm. salts, taken up in little water, very slightly acidified by acetic acid and a fresh solution of $Na_3Co(NO_2)_6$ added. The other part is tested for Na. If necessary the solution is boiled down to a small volume (in porcelain, not in a glass vessel) and a solution of zinc-uranyl acetate is added. When a large excess of K is present, it is advisable to remove this element by means of perchloric acid. The prec. is centrifuged off, the solution evaporated to complete dryness and taken up in water.

> This group also contains Li, Rb and Cs. Li interferes with the sodium reaction. Rb and Cs do not. Rb and Cs interfere with the potassium reaction, Li does not. The complete analysis is best carried out with the solid chlorides. Lithium may be detected by extracting the chlorides with a mixture of ethyl alcohol and ether (1 : 1) and testing the extract by means of the flame colour. Verify by evaporating and prec. as Li_3PO_4 by gentle heating with Na_2HPO_4 and KOH. The residue of the alcohol-ether extraction is used for the detection of

s o d i u m. The best way of detecting potassium when Rb and Cs are present is by means of K_2PtCl_6 under the microscope. Note the size of the crystals. C s may be detected besides Rb and K by means of $KAgI_2$ or with H_2SbCl_6 (reagent: 1 gr. $SbCl_3$, 200 ml. HCl 1,19 and 100 ml. water); use the solid chloride of Cs; R b besides K, when Cs is absent, by means of H_2SnCl_6 (reagent: 10 gr. $Na_2SnCl_6,6aq$ in 100 ml. HCl 1,19; heat to boiling, dilute with 100 ml. water and filter off from prec. NaCl; use the solid chloride of Rb). When Cs is present, the only reliable instrument for the detection of Rb is the spectroscope: two red lines at about 6250 Å. The spectroscopic detection of Cs is also very reliable: two blue lines at about 4600 Å.

H. Finally the original substance is tested for $NH_4^{\cdot}$ by boiling with KOH: smell, moist litmus paper. To prevent the formation of NH_3 by saponification of cyanides it may be necessary to add some $HgCl_2$.

[D.] A N I O N S.[1])

The preliminary examination and the testing for kations ought to have given sufficient evidence of the presence of fluorides, silicates, cyanides, phosphates, chlorates, oxalates, charring organic anions and the anions of As, Sb, Cr, Al, Mn etc. When these metallic anions are present, the question arises, whether they will interfere with testing for anions. If so, they must be removed by means of H_2S. The resulting liquid, or the original substance, is now boiled for a quarter of an hour with an excess of sodium carbonate solution and filtered. T h e f i l t r a t e contains

[1]) We still prefer a non systematic course for the detection of anions, although some interesting systematic procedures have been proposed, such as:

Karaoglanov, Z. anal. Ch. **62**, 217 (1923); Ch. Zbl. **1923**, II, 1015.

Karaoglanov and *Dimitrov*, Z. anal. Ch. **63**, 1 (1923); Ch. Zbl. **1924**, I, 499.

Raurich, Anales Soc. Espanola Fisica Quim, **28**, 749 (1930); Ch. Zbl. **1930**, II, 1885.

Montequi, Anales Soc. Espanola Fisica Quim. **30**, 567 (1932); Ch. Zbl. **1932**, II, 2491.

all the anions, but it is tested only for part of them. Small portions of it are t e s t e d f o r :

I. A. Cl′, B r′, I′, C N′ and C N S′ by adding HNO_3 and $AgNO_3$. When CN′ or CNS′ are present in the original substance (CN′ shown by a very weak acid such as H_2CO_3; CNS′ shown by Fe··· and HCl, which reaction is hindered by I′, NO_2′, S″, S_2O_3″ etc.), they are removed by heating the suspension of the silver salts for one hour on the steam bath with H_2SO_4 1 : 1. When the residue is purely white, it is nothing but AgCl. (Confirm, if possible, the presence of Cl′ by the CrO_2Cl_2-reaction in the original substance). When it is yellow, Br′ and I′ may be present at the same time. Then p a r t of the residue is decomposed by Zn and H_2SO_4 (dilute), and the solution is tested for I′ with KNO_2 a n d chloroform and then for Br′ with chlorine water (no excess) and chloroform or with fluorescein.

A n o t h e r p a r t of the residue is tested for Cl′ by heating it to boiling with N/2 KOH and testing the resulting liquid after centrifuging for Cl′ by means of HNO_3 and $AgNO_3$. If possible carry out the CrO_2Cl_2 reaction with the original substance.

When ferro- or ferricyanides were present in the original substance, they are precipitated in this group. Their Ag-salts are not decomposed by H_2SO_4 1 : 1 but like AgCl, they are decomposed by N/2 KOH. So they interfere with the detection of Cl′. Therefore the solution, obtained after the decomposition, is boiled for a long time with H_2SO_4 (about 1 acid : 2 water) to expel all HCN and only then tested for Cl′.

Thiosulphates give a black prec. with $AgNO_3$, which does not interfere with the detection of Cl′ etc.

B. S O₄″ (and S i F₆″) by adding dilute HCl and $BaCl_2$. If necessary, the presence of SO_4″ in the prec. is confirmed by the hepar reaction or by the reaction with mercuric nitrate.

C. N O₂′ an N O₃′ by means of the ring reaction with dilute and with conc. H_2SO_4. It is necessary to remove ClO_3′,

when present, by reduction with SO_2. Small amounts of NO_3' beside a large excess of NO_2' may be detected by removing the latter by means of urea and acetic acid, reducing the nitrates to nitrites by zinc and acetic acid and testing with α-naphthylamine and sulphanilic acid. Complex cyanides and an excess of chlorides interfere with the ring reaction. They can be removed by gentle boiling for some time with a Ag_2SO_4-solution.

D. A c e t a t e and f o r m a t e by distilling with H_2SO_4 1 : 2. A substantially acid distillate is obtained. The distinction between the two is accomplished by: the reducing power of formate (slightly acid hot $HgCl_2$), the smell, or the cacodyl reaction with the original substance. When SO_3'' is present, it must be oxidised beforehand with no more cold iodine water than is necessary.

II. T h e   o r i g i n a l   s u b s t a n c e   i s   t e s t e d   f o r :

A. SO_3'', S_2O_3'' and S'', together by the hepar reaction in a closed tube (beware of CNS'). They are distinguished by their behaviour towards 2N H_2SO_4, especially the smell of the decomposition products. Sulphides and thiosulphates react with NaN_3 and I_2; sulphites do not.

B. CO_3'' by treating with HCl and leading the gas into a solution of $Ca(OH)_2$. When SO_3'' is present it is oxidised beforehand with iodine, or chromic acid is used for the decomposition.

C. BO_2' by the flame colour, either with $KHSO_4$ and CaF_2 on a platinum wire, or, when copper is present, by means of methyl alcohol and conc. sulphuric acid.

[E.]   RESIDUE, INSOLUBLE IN AQUA REGIA.

May be present: SiO_2 and silicates, CaF_2, $BaSO_4$, $SrSO_4$, $PbSO_4$, SnO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, Sb_2O_5, silver halides, silver-cyanogen compounds and other complex cyanides.

(And a great many compounds of less general elements, vide infra).

Carry out the following operations:

a. B l o w p i p e   a n a l y s i s   o n   c h a r c o a l: very useful for this kind of substances. The substance is now better not mixed with sodium carbonate but with potassium oxalate.

G l o b u l e s of Ag, Pb, Sb, Sn; dissolve in conc. HNO_3 etc.

H e p a r   r e a c t i o n: SO_4''.

b. F l a m e   c o l o u r after reduction in a luminous flame and moistening with HCl: green Ba; red Sr.

c. M e l t   o n   a   n i c k e l   c r u c i b l e   l i d   w i t h   s o l i d   K O H (in view of Sb better not NaOH). Extract with water and test for Sn, Sb, Al, Cr and for SiO_2 (if necessary after volatilisation as SiF_4). The residue is tested for Fe.

d. F l u o r i n e   r e a c t i o n by means of SiO_2 and conc. H_2SO_4 in lead capsule.

e. C y a n i d e   r e a c t i o n by prolonged boiling with sodium carbonate.

> Moreover the residue may contain:
>
> a. WO_3.
>
> β. Ti, Zr, Cb and Ta-compounds.
>
> γ. Ignited oxides of Ce, Th, La etc.
> All these substances are decomposed by melting with KOH. Thoroughly extract with cold water and separate in the centrifuge:
>
> 1. R e s i d u e: Zr, Ce, Th, La etc. (and perhaps some Cb and Ta, who do not interfere). It is dissolved in some drops of conc. H_2SO_4, the excess of H_2SO_4 removed, taken up in hot water and reprecipitated by NH_3. In this prec. Zr, Ce, Th, La etc. are detected as described sub C.
>
> 2. S o l u t i o n: W, Ti, Cb and Ta. In this solution, the presence of W is shown by the yellow colour of the prec. with HCl and by the lively blue colour with Zn and HCl. Cb gives a more dull blue colour. Ti is detected by H_2SO_4 and H_2O_2 or with chromotropic acid and $SnCl_2$.

The detection of Ta is best carried out by bringing a drop of the KOH-extract together with a drop of HF-solution on a cellon (acetyl cellulose) object glass: crystalline prec. of K_2TaF_7, fine needles. When W and Ti are absent, the detection of Cb is easily possible by acidifying with conc. HCl and adding a solution of tannin (orange-red colour). When W or Ti are present, this reaction is useless. In that case Cb is very difficult to detect. We recommend in that case the microchemical reaction as $Na_8Cb_6O_{19}$, relatively large crystals, about 0,1 mm., whereas the crystals of the corresponding tantalate are considerably smaller.

LIST OF REAGENTS.

The solutions are contained in 30 ml. bottles provided with a pipette stopper, closed with small ends of rubber tubing and a small cork. The solid reagents are contained in 30 ml. wide neck stoppered bottles. They are brought together on a special rack, consisting of several tiers of reagent shelves. The reagents include the following:

Solutions:

1. Hydrochloric acid; 2N.
2. Sulphuric acid; 2N.
3. Nitric acid; 2N.
4. Acetic acid; 2N.
5. Tartaric acid; 5 %.
6. Oxalic acid; 5 %.
7. Ammonia; conc.
8. Potassium hydroxide; 2N.
9. Sodium carbonate; 5 %.
10. Hydrogen peroxide; 3 %.
11. Bromine water; satur.
12. Potassium ferrocyanide; 5 %.
13. Sodium azide; 2,5 %.
14. Iodine; 0,1 N in dil. KI.
15. Zinc sulphate; 10 %.
16. Amm. mercuric sulphocyanate; 30 gr. $HgCl_2$, 33 gr. NH_4CNS in 100 ml. water.
17. Copper sulphate; 0,5 %.
18. Lead acetate; 4 %.
19. Stannous chloride with tin; 5 %.
20. Zinc uranylacetate, acc. to Kolthoff.
21. Methyl violet; 0,1 % in water.
22. Cacotheline; 0,25 % in water.
23. Rhodamine-B; 0,25 gr. rhod.-B, 75 gr. KCl in 500 ml. 2N HCl.
24. Thymol blue; 0,04 % in alcohol.
25. Amyl alcohol.
26. Phenol; 5 % in water.
27. Manganous sulphate; 2 %.
28. Diphenylcarbazide; 1 % in alcohol.
29. Aniline.

30. Tetramethyl-diamino-diphenyl-methane; 0,5 % in alcohol with 5 % acetic acid.
31. Dimethylglyoxime; 1 % in alcohol.
32. Ethyl alcohol; 96 %.
33. Benzidine acetate; 1 % in water and acetic acid to dissolve.
34. Alizarin-S; 0,2 % in water.
35. Titan yellow; 0,05 % in alcohol.
36. Carbon tetrachloride.

Solid substances:

37. Sodium acetate.
38. Ammonium chloride.
39. Ammonium sulphocyanate.
40. Ammonium molybdate.
41. Sodium cobaltinitrite.
42. Silver nitrate.
43. Powdered quartz.
44. Sodium fluoride.
45. Sodium nitrite.
46. Sodium arsenite.
47. Potassium periodate.
48. Fluorescein.